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Studies on the Reactions of Polycyclic Aromatic Hydrocarbons With Nitrogen-Dioxide in Aprotic Solvents.

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STUDIES ON THE REACTIONS OF POLYCYCLIC AROMATIC HYDROCARBONS WITH NITROGEN DIOXIDE IN APROTIC SOLVENTS

A Dissertation

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Thanks also to Prof. Steven F. Watkins and Dr. Frank R. Fronczek for the crystallographic determinations; to Rafael Cueto for the FTIR spectra; to Marcus Nauman for assisting with software and hardware manipulation of NMR spectrometers; to Ming-Dan Wu for assisting with the nitrogen dioxide calibration plot; and, to Susan Finley for freeing my hands for labwork.

My sincere gratitude to the Coates Memorial

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Finally, I would like to thank my friends and colleagues, Thomas Lachoki, Christopher Kennedy, Juan Moreno, Ming-Dan Wu and Rafael Cueto for making this an enjoyable time. Many others, faculty, staff and students, go unnamed but not unappreciated.

To my wife Maria,

to my mother Elizabeth, and,

to my father Juan Jose.

FOREWORD

This dissertation contains four chapters that investigate the reactions of nitrogen dioxide with selected polycyclic aromatic hydrocarbons.

The first chapter, "Anomalous Nitration of Fluoranthene with Nitrogen Dioxide" was authored by Mr. Giuseppe L. Squadrito, Dr. Daniel F. Church and Dr. William A. Pryor. The manuscript was submitted on June 3, 1987 and published in October 14, 1987 (J. Am. Chem. Soc. 109, 6535-6537). In addition, some of the results reported in this chapter were presented at the 194th American Chemical Society National Meeting in New Orleans, during August 30 - September 4, 1987 (Organic Abstract # 17) and a preliminary account on the mutagenicity of nitrofluoranthenes was presented at the 19th Annual Meeting of the Environmental Mutagen Society in Charleston, during March 27 - 31, 1988. This chapter reports on the free radical and the electrophilic ionic nitration of the non-alternant hydrocarbon fluoranthene. A multiple step addition-elimination mechanism is proposed for the free radical nitration.

The second chapter, "A Dichotomy in the Nitration of Fluoranthene with NO_2/N_2O_4: Mechanistic and Toxicological Implications" will be submitted for publication to the Journal of the American Chemical Society. This chapter is

a continuation of the first chapter.

The third chapter, "The Reaction of Anthracene with Nitrogen Dioxide Revisited" will be submitted for publication to the Journal of Organic Chemistry. This chapter reports on the free radical mechanism of nitration of anthracene, the possible involvement of charge-transfer complexes, and the relevance of the free radical nitration mechanism to atmospheric reactions.

The fourth chapter, "Free Radical Nitration of Naphthalene with Nitrogen Dioxide in CCl_4" was authored by Mr. Giuseppe L. Squadrito, Dr. Frank R. Fronczek, Dr. Daniel F. Church and Dr. William A. Pryor. The manuscript was submitted in August 31, 1988 for publication to the Journal of Organic Chemistry. This chapter reports on the free radical mechanism of nitration of naphthalene and its relevance to atmospheric reactions.

Finally, an Appendix, that details experimental procedures pertaining to the four preceding chapters, has been included. Reasons of journal space economy preclude going into much detail at the time the manuscripts were (will be) submitted for publication. This Appendix includes NMR and FTIR data for several nitro-polycyclic aromatic hydrocarbons and details of the implementation of an NMR technique for selective polarization transfer from ^{1}H to ^{13}C. Some of the spectra presented in this appendix will be part of a future publication on the assessment of

the mutagenicity of the nitrofluoranthenes, others were included in a recent Grant Proposal for adding a new spectrometer to the Chemistry NMR Facility.

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ABSTRACT

There is recent evidence that free radical nitration reactions occur in polluted urban air, and that the nitrated polycyclic aromatic hydrocarbons (NO_2-PAH) produced by this reaction pathway account for a substantial amount of the total NO_2-PAH found in ambient particulate organic matter. The nitration of PAH with nitrogen dioxide in solvents of low polarity has been studied as a model for the reactions occurring in the atmosphere (gas phase).

While vast amounts of data are available for the electrophilic ionic nitration and its mechanism of reaction is considered well-established (and often included in sophomore Chemistry books), the literature documents relatively few reports on the mechanism of reaction of PAH with nitrogen dioxide. Our studies indicate that: (1) a free radical mechanism operates in solvents of low dielectric constant (e.g. CCl_4) and becomes less important as the dielectric constant is increased ($CHCl_3$, CH_2Cl_2, THF, CH_3CN, CH_3NO_2), (2) Bronsted and Lewis acids, and lower temperatures promote the electrophilic ionic reaction pathway, (3) the free radical mechanism involves metastable adducts of the PAH and two to four nitrogen dioxide equivalents, (4) the radical reaction yields nonconventional substitution

patterns of dinitro-PAH even at low conversions (e.g. 1,2- and 1,3-dinitrofluoranthenes and, 1,3- and 2,3-dinitronaphthalenes), (5) the radical reaction of anthracene with nitrogen dioxide yields cis- and trans-9,10-dinitro,9,10-dihydroanthracene, which are isolable, (6) in radical nitration, the nitro-group does not have a strong deactivating effect towards further nitration as in electrophilic ionic nitration, in fact, its effect in radical nitration is frequently that of slight activation.

1. NITRO-POLYCYCLIC AROMATIC HYDROCARBONS: A LEGACY OF THE TWENTIETH CENTURY

Before the advent of diesel and gasoline engines, the main sources of nitrogen oxides in the troposphere (0 to 12 Km above the Earth's surface) were restricted to microbial activity, input from the stratosphere,[1] and occasional forest fires. Today, these sources account only for ca. 40% of the total production of nitrogen oxides. The main sources of nitrogen oxides are now fossil fuel combustion and biomass burning,[1] with a combined input of approximately 3.3×10^{10} Kg/yr. Thus, the nitrogen cycle has been subjected to a substantial change.

Over the last decade, nitro-polycyclic aromatic hydrocarbons (nitro-PAH) have received increasing attention from the scientific community and from regulatory and health officials. Large amounts of PAH and nitro-PAH are produced from several anthropogenic activities including diesel[2] and gasoline[3] engine exhausts, soot from wood-burning residential heating,[3] coal fly ash,[4] and aluminum smelting effluent condensates.[5]

2. EVIDENCE FOR NEW NITRO-POLYCYCLIC AROMATIC HYDROCARBON-PRODUCING ROUTES: FREE RADICAL ATMOSPHERIC REACTIONS OF NITROGEN DIOXIDE AND POLYCYCLIC AROMATIC HYDROCARBONS.

Recently, 2-nitrofluoranthene and 2-nitropyrene have been identified in ambient particulate organic matter (POM).[6] These isomers are formed in very low yields, or not formed at all, by the common nitration proceedures (e.g. nitric acid in acetic acid or acetic anhydride). Unusually low 1-nitronaphthalene/2-nitronaphthalene ratios have also been reported in ambient POM,[7] contrasting with the corresponding ratios obtained by electrophilic ionic nitration. The unexpected discovery of 1,3-dinitronaphthalene[8] in ambient POM cannot be accounted by addressing an ionic electrophilic mechanism of nitration. Thus, there is currently strong evidence that part of the nitro-PAH present in the urban environment arises from atmospheric reactions.

The atmospheric reactions of nitrogen oxides with PAH may have an important role in the formation of nitro-PAH. Since we have focused mainly on the thermal (dark) nitration of PAH, our results are more relevant to night-time atmospheric chemistry.

3. THE REACTION OF POLYCYCLIC AROMATIC HYDROCARBONS WITH NITROGEN DIOXIDE IN APROTIC SOLVENTS

Nitrogen dioxide* (NO_2) has been recently recognized as an effective nitrating reagent.[9,10] The study of the reaction of NO_2 with PAH in solvents of low polarity, conditions that model the gas phase counterpart of this reaction, may provide explanations to the observation of the anomalous nitration products found in ambient POM. More complete studies of the effect of solvent polarity, the effect of temperature and of a selected added species may provide additional insights into the little understood mechanisms of the reactions of NO_2 and PAH.[11] The chemical literature documents some scattered fragmentary reports, many times controversial, on the reactions of NO_2 with PAH. This field of study has long been neglected probably due to an early publication in which it was concluded that NO_2 has limited synthetic applications.[12] The absence of a comprehensive comparative work, like those conducted by Dewar with nitric acid in acetic anhydride and by Olah with nitronium ion salts, is regrettable.

4. IDENTIFICATION OF NOVEL NITRATION PRODUCTS

The high toxicity of nitro-PAH requires that these

compounds be handled in very small amounts and with extreme caution. Very sensitive techniques are therefore desirable for their identification. Mass spectrometry, usually in combination with gas chromatography, can be used in the nanogram scale. This technique indicates how many nitro groups have been introduced on the aromatic nucleus. The position of substitution can be established by interpreting the high resolution ^{1}H-NMR spectra of the nitro-PAH. High resolution ^{1}H-NMR is also a very sensitive technique that requires only submilligram quantities. The use of two-dimensional techniques is very convenient because the nitro-PAH commonly display tightly coupled spectra restricting the use of conventional decoupling and saturation experiments to one or two protons per molecule. Throughout this study, a combination of ^{1}H-NMR techniques was used as identification tools, and to assign as many resonances as possible. A thorough study of the ^{1}H-NMR spectra of these nitro-PAH ensures future identification of their metabolites, which are present in very small amounts.

5. 1D AND 2D NMR TECHNIQUES EMPLOYED FOR THE IDENTIFICATION OF NITRO-PAH

The availability of ^{1}H-NMR techniques of various degrees of sophistication greatly facilitate the analysis

of complicated spectra. Brief descriptions of the techniques employed and of the ways to interpret the data are explained below. A sensitive ^{13}C-NMR technique (selective-INEPT, also termed INAPT) is also described.

5.1 THE HOMODECOUPLING EXPERIMENT

In this experiment, the proton decoupler (on a low power setting) is placed over a resonance. A change in the multiplicity of one or more resonances indicate that they are J-coupled (scalar coupled or coupled through-bond) to the irradiated resonance.

5.2 THE NUCLEAR OVERHAUSER EFFECT (NOE) EXPERIMENT

A different type of coupling is termed dipole-dipole coupling. In contrast to the J-coupling that is a through-bond type of coupling, the dipole-dipole coupling is a through-space coupling. The dipole-dipole coupling is strongly dependent on the distance between the nuclei, decaying with the inverse of the six-power. Thus, protons that are not bonded to each other but because of the overall shape of the molecule are constrained to be close in space, will experience dipole-dipole coupling. The NOE experiment is similar to the homodecoupling experiment but for NOE the decoupler is turned on for ca. 2 s. and then

is turned off immediatly before starting acquisition (gated decoupling). The perturbation caused to the system is termed saturation, meaning that the population difference between the states involved in some transitions is eliminated. The attempts of the system to stay at thermal equilibrium are manifested as forced population differences between other states causing changes in intensity in the neighboring resonances. These changes are usually small (a few percentage units) and much easier to observe by subtracting the results of the experiment in which the resonance of interest was saturated from those of a control experiment. This variation of the technique is usually referred as NOE-Difference. The automation program NOEDIFF, provided with the Brucker spectrometers software was employed for this purpose.

5.3 THE ^{1}H-^{1}H COSY (COrrelation SpectroscopY) 2D EXPERIMENT

This experiment correlates chemical shifts with J-coupling. The data are generally presented as a square plot, symmetrized along the diagonal. The projections of the diagonal over the sides of the square are the 1D spectrum of the examined compund. Off-diagonal peaks denote the protons that are J-coupled to each other. The experiment normally considers only relatively big coupling

constants (larger than 2 Hz) unless it is optimized for the observation of smaller couplings by including an additional waiting period in the pulse train. This variation of the COSY experiment is termed "long-range COSY".

The ^{1}H-^{1}H COSY technique does not require non-overlapping resonances to unambiguously determine the sets of coupled protons and overcomes the limitations of the simple homonuclear decoupling experiment. The automation program COSY or COSYLR, provided with the Brucker spectrometers software, were employed for this purpose.

5.4 The Selective-INEPT Experiment (Selective version of the Insensitive Nuclei (^{13}C) Sensitivity Enhancement by Polarization Transfer (from ^{1}H))

This is a sensitive ^{13}C-observed technique in which polarization is transferred from ^{1}H to ^{13}C via J-couplings. In the selective version of this experiment, the decoupler is placed over the proton of choice and its ^{13}C-environment can be established by optimizing the experiments for polarization transfer through either one bond or three bonds. Only the carbon atoms with the given couplings will appear in the spectrum. The experiment is particularly attractive for the observation and assignment

of quaternary carbons. In this regard, besides the sensitivity enhancement inherent to the polarization transfer experiment, the scan repetition rate is controlled by ^{1}H- rather than by the much longer ^{13}C-relaxation times.

6. PURPOSE OF THIS WORK

The purpose of this work is to provide a better understanding of the reactions of NO_2 with PAH that will help assess the health risks of exposure to nitro-PAH formed under environmentally relevant conditions.

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* Throughout this work, nitrogen dioxide (NO_2) and dinitrogen tetraoxide (N_2O_4) have been used interchangeably, unless specified otherwise, for what is the equilibrium mixture.

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CHAPTER I. Anomalous Nitration of Fluoranthene With Nitrogen Dioxide In Carbon Tetrachloride

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Dear Sir:

I am writing to you in reference to the article "Anomalous Nitration of Fluoranthene with Nitrogen Dioxide in Carbon Tetrachloride" published in the Journal of the American Chemical Society, 1987, 109, 6535-37. I am the first author of this manuscript and I would like to use a reprint in my Ph.D. dissertation.

Please, forward permission to reprint the manuscript. I will appreciate your prompt reply.

Sincerely,

G. Squadrito

Giuseppe L. Squadrito
Biodynamics Institute
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ABSTRACT

As a part of a continuing study on the reaction of polycylic aromatic hydrocarbons, we have examined the reaction of fluoranthene as a probe for distinguishing between radical and electrophilic substitution. The product distribution of the reaction of fluoranthene with NO_2/N_2O_4 shows a marked solvent dependency. At low conversions in CCl_4, the products are 2-nitrofluoranthene (53.7%; 2NF), 3NF (23.7%), 1,2-dinitrofluoranthene (12.3%; 1,2-DNF), 1,3-DNF (7.4%), and other products (2.8%). In CH_2Cl_2, 3NF (69.0%), 8NF (23.0%), 7NF (3.2%), 1NF (2.6%) and 2NF (2.3%) are formed. These observations are rationalized as a change from an ionic to a homolytic mechanism when the reaction is carried out in a solvent of low polarity.

In CH_2Cl_2, NO_2/N_2O_4 cleanly nitrates polycyclic aromatic hydrocarbons (PAH's) and is the method of choice for the synthesis of mononitrated derivatives.[1] The mechanism of the reaction of NO_2/N_2O_4 with PAH in aprotic solvents, however, remains controversial. Mechanisms involving free-radical attack,[2] electron-transfer[3] and electrophilic substitution[4] have been proposed.

In order to obtain additional insights into the mechanism of reaction of NO_2/N_2O_4 with PAH, we have examined the nitration of fluoranthene, 1, a non-alternant hydrocarbon. Frontier orbital calculations indicate that the positional reactivity in 1 will vary depending upon the nature of the attacking species;[5-7] for example, the order of reactivity for homolytic attack is predicted to be 3 >1 >7 >8 >2 , while the order for electrophilic attack is expected to be 3 >8 7 >1 >2. Thus, 1 may provide a probe for distinguishing between radical and electrophilic substitution pathways.

Experimental data for electrophilic substitution[8] (Table I) affords an order of positional selectivity 3 >8 >7 >1 >2, in agreement with the theoretical prediction. The only previous data for radical substitution on 1

	Reagents					
Products[a]	NO_2/CCl_4[b]	NO_2/CH_2Cl_2[c]	NO_2/CH_2Cl_2[e]	HNO_3/Ac_2O[g]	HNO_3/Ac_2O[h]	N_2O_5/CCl_4[i]
1NF	1.1 ± 0.3	d	2.6 ± 0.3	11.1 ± 3.3	8.6 ± 0.4	-
2NF	53.7 ± 2.3	-	2.3 ± 0.1	-	f	80
3NF	23.7 ± 3.0	63	69.0 ± 1.1	43.5 ± 5.8	49.3 ± 0.1	-
7NF	0.7 ± 0.2	d	3.2 ± 0.0	18.4 ± 3.9	11.0 ± 0.1	-
8NF	1.0 ± 0.1	27	23.0 ± 0.8	27.0 ± 5.8	31.3 ± 0.4	-
1,2-DNF	12.3 ± 1.1	-	f	-	f	20
1,3-DNF	7.4 ± 0.9	-	f	-	f	-

Table I. Nitration of Fluoranthene Under Different Conditions. [a]Percentage distribution, quantified by GC on a 30-m DB-17 capillary column by using flame ionization detector unless specified otherwise. [b]Our work, using conditions specified in ref 10. [c]Reference 1, room temperature. [d]1NF and 7NF reported together as 10%. [e]Our work, conditions as in b but using CH_2Cl_2 as solvent. [f]Less than 0.5%. [g]Reference 8, 0°C; quantified by IR. [h]Our work, conditions as in g but quantification done by GC. [i]Reference 9, 25°C.

concerns its nitration by N_2O_5.[9] These data were interpreted in terms of the initial σ-complex resulting from the attack at the 3-position by the NO_3 radical coupling with NO_2 at the 2-position to give the unstable 3-nitrato-2-nitro-2,3-dihydro- fluoranthene which aromatizes by losing a molecule of nitric acid.

We have studied the nitration of 1 under a variety of conditions (Table I). In CH_2Cl_2, NO_2/N_2O_4 displays the same positional order of reactivity as does HNO_3 in Ac_2O, the classical reagent for electrophilic nitration. Thus, NO_2/N_2O_4 appears to react by an electrophilic mechanism in CH_2Cl_2;[1] however, we also have found that a substantial amount of 2-nitrofluoranthene (2NF) is formed in CH_2Cl_2, which appears to have been previously overlooked.[1]

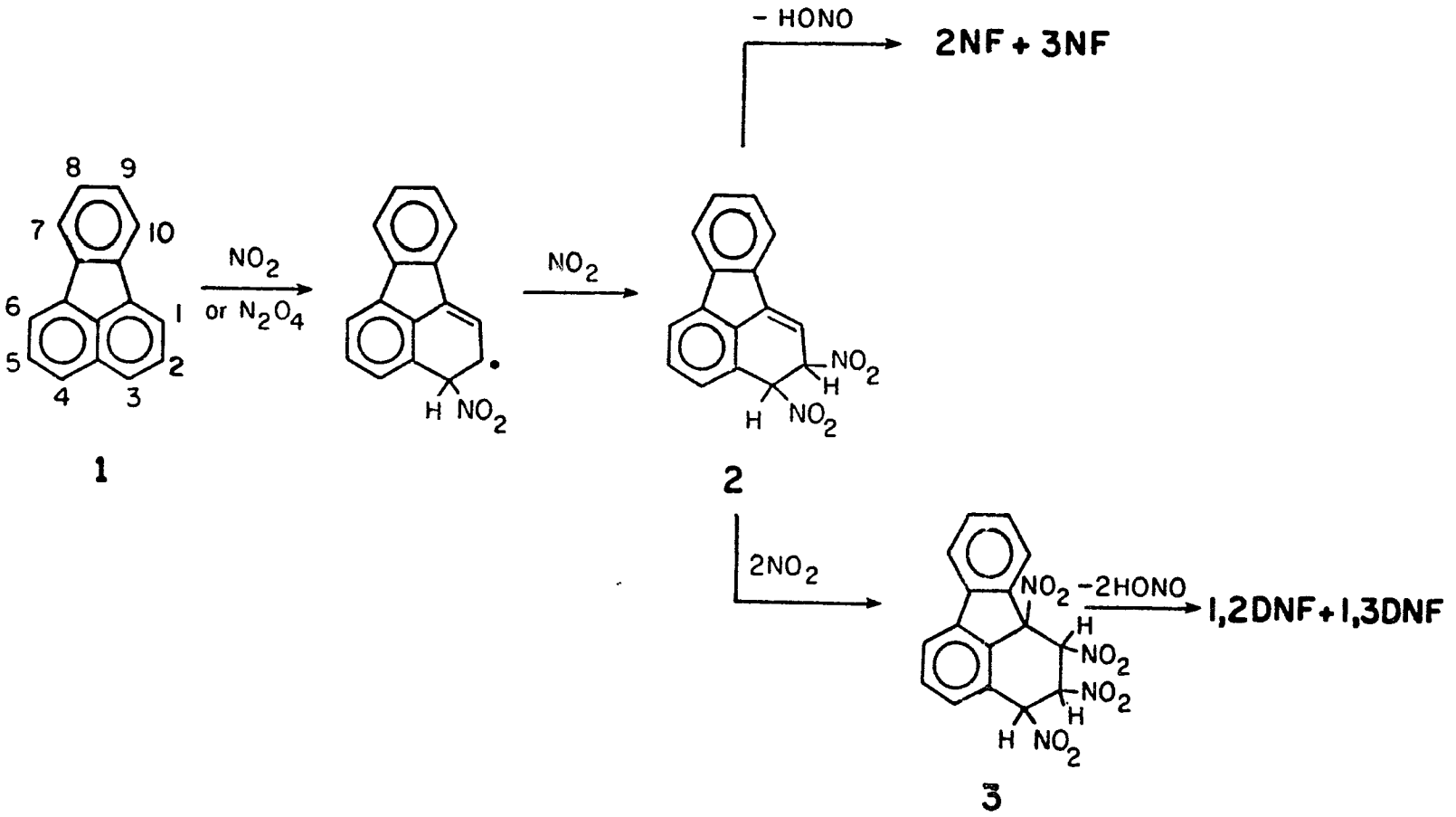
Since homolytic processes should be facilitated relative to ionic ones as the solvent polarity is decreased, we also studied the nitration of 1 in CCl_4.[10] Both 2NF and 3-nitrofluoranthene (3NF) were isolated as the major products from the reaction mixture and identified by ^{1}H-NMR and GC/MS. Small amounts of 1-nitrofluoranthene (1NF), 7-nitrofluoranthene (7NF) and 8-nitrofluoranthene (8NF) were detected by GC/MS and characterized by comparison of their retention times and fragmentation patterns to those of authentic samples. Traces of a fluoranthene quinone also were detected. Two dinitrofluoranthenes were isolated, and ^{1}H-NMR indicates

that disubstitution occurred in one of the rings of the naphthalene-like moiety. One of these disubstituted compounds is 1,2-dinitrofluoranthene (1,2DNF), based on its proton-proton nuclear Overhauser effect (NOE)[9] and confirmed by single crystal X-ray diffraction analysis.[11] The other dinitro species is 1,3-dinitrofluoranthene (1,3DNF), as indicated by the absence of NOE between the downfield singlet and H-10 using 2NF as a model, and by characteristic downfield shifts of the peri and bay protons near the in-plane nitro-groups.

Thus, the distinctive features of the nitration in CCl_4 are the formation of much greater yields of 2NF and much lower yields of 8NF than are obtained under electrophilic conditions and the production of modest yields of dinitrofluoranthenes even at low conversions. Furthermore, disubstitution to produce dinitrofluoranthenes always occurs in the same ring, in one case leading to an unexpected 1,2-dinitro-species.

Theoretical models involving an intermediate σ-complex[6,7] cannot account for the product distribution unless a second intermediate were formed, as depicted in Scheme I. Attack at the 3-position by NO_2 (or N_2O_4) and subsequent addition of a second NO_2 (perhaps in a cage) leads to the dinitrodihydro-intermediate 2. Intermediate 2 can eliminate a molecule of nitrous acid to form either 2NF or 3NF, determining the mononitrated product

Scheme I


- HONO
2NF + 3NF
8
9
7
10
6
1
5
2
4
3
NO_2
or N_2O_4
H NO_2
NO_2
NO_2
H
H NO_2
1
2
$2NO_2$
NO_2 -2HONO
1,2DNF + 1,3DNF
H
NO_2
NO_2
H
H NO_2
3

specificity. The formation of 2NF may be favored over 3NF due to a small peri interaction between the nitro-group and H-4 in the latter case. Alternatively, 2 can react further with two more equiv of NO_2 to form the tetranitrotetrahydro-intermediate 3, which can aromatize by losing two molecules of nitrous acid to form 1,2-DNF and 1,3-DNF.[12] This mechanism is similar to that proposed by Zielinska et al.[9] for the reaction of 1 with N_2O_5; however, in their case the loss of nitric acid is under thermodynamic control so that products with a substituent at the 3-position are not observed.

Thus, 1 allows a distinction between two different mechanisms of reaction of NO_2/N_2O_4. The isomer distribution in CH_2Cl_2 follows the electrophilic substitution pattern predicted from theory, whereas the product distribution in CCl_4 can best be rationalized by a radical mechanism for the nitration.[13] If 2NF is considered as a marker for radical nitration as we suggest, then the homolytic pathway, although not predominant, may be a minor path even in CH_2Cl_2 where some 2NF is formed.

Our results may be of environmental relevance since the uninitiated reaction of NO_2/N_2O_4 with 1 in a solvent of low polarity leads to the formation of nitroaromatics that are potential mutagens.[14] In this regard, 2NF was recently detected among the major nitro-PAH present in

ambient air samples;[15-17] however, this product did not appear to arise from either combustion processes or direct electrophilic nitration, and atmospheric radical reactions initiated by N_2O_5 or hydroxyl radicals have been proposed.[15-18]

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(10) In a typical experiment, 6 mL of a CCl_4 solution of NO_2/N_2O_4 (2.8 mM NO_2 and 45 mM N_2O_4) was added to 2 mL of a 0.15 M solution of fluoranthene under nitrogen at 25°C.

Quantification of products was done by GC using a flame ionization detector after the evaluation of relative response factors. The product distribution remained constant between 0 and 15% conversion (0 to 10 h) with a material balance of 90.0 ± 5.3% (triphenylene as internal standard).

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(12) The dinitrofluoranthenes cannot be being formed via heterolytic nitration of the mononitrofluoranthenes because the latter are expected to be several orders of magnitude less reactive than the parent hydrocarbon; furthermore, a different disubstitution pattern would be expected.

(13) One of the referees suggested an alternative mechanism in which a cationic σ-comlex is involved; however, we have preliminary data that show that nitrofluoranthene reacts with NO_2/N_2O_4 at a faster rate than does fluoranthene itself, excluding an electrophilic mechanism.

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CHAPTER II. A DICHOTOMY IN THE NITRATION OF FLUORANTHENE WITH NO_2/N_2O_4: MECHANISTIC AND TOXICOLOGICAL IMPLICATIONS

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ABSTRACT

The nitration of fluoranthene with nitrogen dioxide can occur by two distinctive reaction pathways. The reaction products have been identified by GC/MS, 1D and 2D NMR techniques, and, in one case (1,2-dinitrofluoranthene) by a single crystal X-ray analysis. In solvents with dielectric constant lower than that of CH_2Cl_2 and in the absence of acid catalysis, the exclusive reaction pathway is homolytic in nature. The products of the homolytic reaction pathway can be interpreted as arising via a multiple step addition-elimination mechanism. The formation of 2-nitrofluoranthene (the major product in CCl_4, but absent under electrophilic nitration conditions) and the unusually large amounts of the unexpected 1,2-dinitrofluoranthene and 1,3-dinitrofluoranthene can be adequately explained on the basis of this mechanism. In contrast, in solvents with higher dielectric constants, the main reaction pathway gives a product distribution in agreement with that predicted by molecular orbital calculations using a cationic σ-complex model, indicating an electrophilic ionic process. A noticeable difference in product distribution as the mechanism changes from ionic to free radical was expected because fluoranthene is non-alternant, and its radical σ-complexes have a half-filled,

either bonding or antibonding, molecular orbitals. The half-filled molecular orbital changes the stability of the radical σ-complexes with respect to the corresponding cationic σ-complexes, in contrast with alternant hydrocarbons which order in stability is maintained because the half-filled molecular orbital is nonbonding. The ionic reaction is catalysed by Lewis and Bronsted acids, particularly in CH_2Cl_2, and is inhibited by non-nucleophilic bases like 2,6-di-tert-butylpyridine. At temperatures lower than room temperature, the ionic reaction pathway predominates, even in CCl_4. 2-Nitrofluoranthene is a marker for the free radical nitration of fluoranthene, and, its presence in polluted tropospheric air suggests free radical nitration by NO_2 occurs under atmospheric conditions.

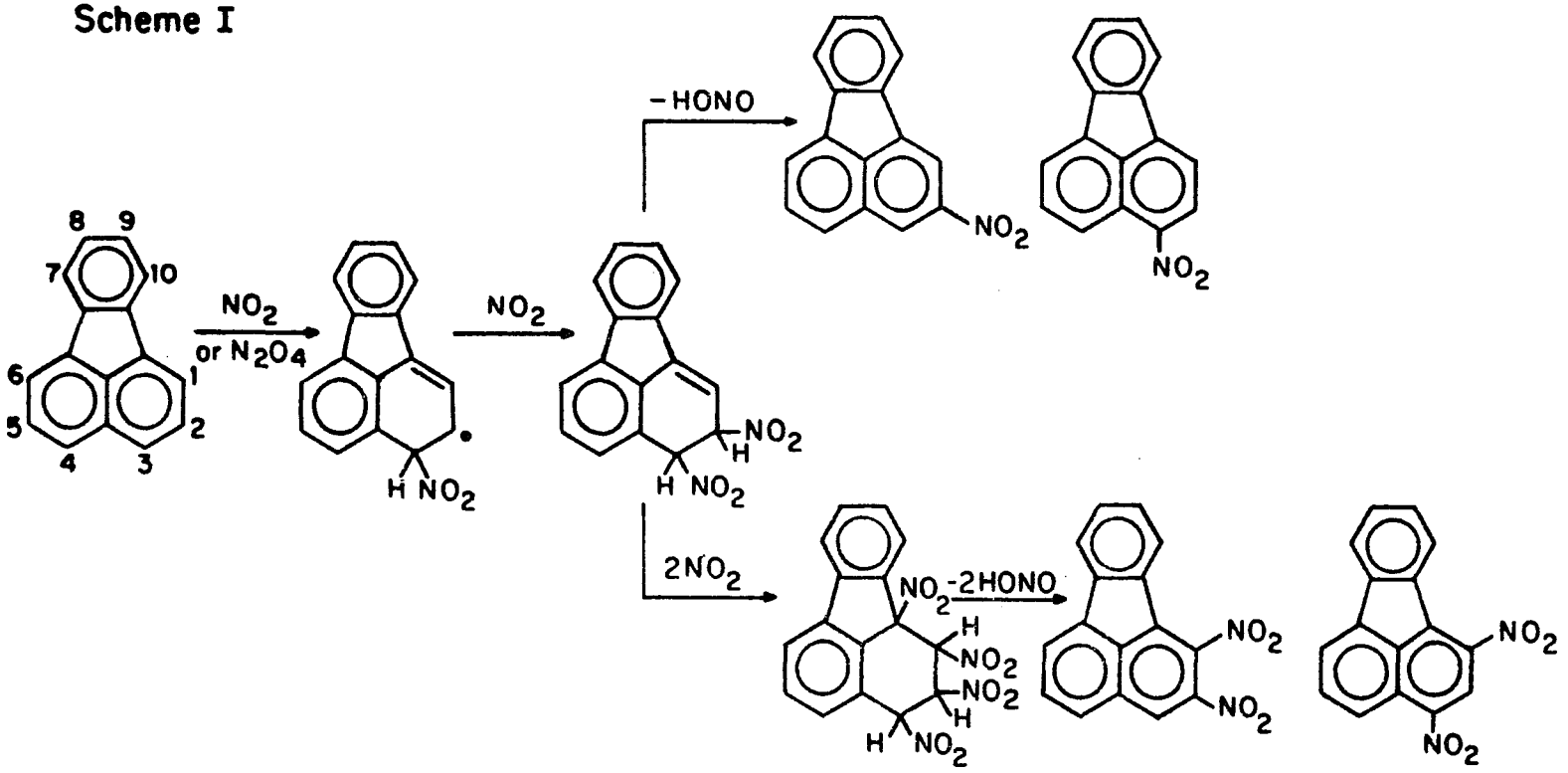
The reactions of polycyclic aromatic hydrocarbons (PAH) with nitrating agents have received much attention recently due to the potential for the formation of nitro-PAH in urban atmospheres[2-5] and the mutagenic and/or carcinogenic properties of these compounds.[6,7] Nitro-PAH are thought to arise from a variety of human activities including fossil fuel combustion and biomass burning. However, the origin of certain nitro-PAH that are present in airborne particulate matter cannot be explained in terms of the conventional ionic nitration mechanism.[4,8,9] For example, 2-nitrofluoranthene (2NF), despite being the most abundant and ubiquitous nitro-PAH pollutant,[4,8,9] has not been observed in combustion emissions[3] or under various nitration conditions.[10,11] Recently, 2NF has been identified under homolytic nitration conditions,[12-15] and it was proposed that 2NF arises from radical reactions in polluted tropospheric ambient air.[4,8,9,13,14]

Despite the numerous works devoted to nitration of PAH, reports on the reaction of PAH with NO_2/N_2O_4 are often controversial, and mechanisms involving electron transfer, radical, or electrophilic substitution have been proposed.[16] We have recently reported on the radical nitration of fluoranthene, 1, with NO_2/N_2O_4 in CCl_4.[14] We proposed the use of 1 as a mechanistic probe for distinguishing between radical and electrophilic nitration because, being a non-alternant hydrocarbon, it gives a

markedly different product distribution according to the type of reaction mechanism. Thus, the positional reactivity found with nitronium ion-mediated nitration follows the order *3 > 8 > 7 > 1 > 2*, in agreement with the theoretical calculations involving an intermediate σ-complex that dictates the regioselectivity of the process.[17-19] In contrast to the general behavior of cationic σ-complexes which readily loss their highly acidic proton and rearomatize,[20] radical σ-complexes preferentially undergo radical-coupling rather than aromatization via hydrogen-atom abstraction.[12-15] Indeed, when the σ-complex theoretical model is applied to radical addition the order *3 > 1 > 7 > 8 > 2* is predicted;[17-19] however, the distribution of nitrofluoranthenes obtained experimentally has to be interpreted as multiple addition-elimination occurring after the formation of the radical σ-complex.[14] These observations lead us to propose 2NF as a marker for radical nitration (Scheme I). In addition, the radical nitration of 1 leads to the facile formation of dinitrofluoranthenes of unusual substitution pattern, even at low conversions. The observed substitution patterns of these dinitrofluoranthenes can also be explained by the multiple addition-elimination mechanism.

In order to help unravel the current mechanistic problem of the nitration of PAH with NO_2/N_2O_4 we have conducted a solvent study, a study of the effect of

Scheme I


8
9
7
10
6
1
5
2
4
3
NO_2
or N_2O_4
H NO_2
NO_2
H
NO_2
H NO_2
-HONO
NO_2
NO_2
$2NO_2$
NO_2-2HONO
H
NO_2
NO_2
H
H NO_2
NO_2
NO_2
NO_2
NO_2

selected added species, and a study of the temperature effect on the product distribution of the reaction of 1 with NO_2/N_2O_4 under these conditions.

EXPERIMENTAL SECTION

Materials. Fluoranthene (Aldrich, 98%+ GC-area%) was used without further purification. Anhydrous nitric acid was distilled prior to use from concentrated nitric acid (Mallinkrodt) and sulfuric acid (Baker). Methane sulfonic acid (Eastman Kodak) and nitrosonium tetrafluoroborate (Aldrich) were used as received. HPLC-grade carbon tetrachloride (Baker) was dried over potassium carbonate and/or distilled under dry nitrogen. Tetrahydrofuran (QO Chemicals) was distilled from sodium under nitrogen. Acetonitrile (Mallinkrodt) and nitromethane (Aldrich) were dried over sodium sulfate and distilled. Dinitrogen tetroxide (MCB) was distilled until a pure white solid was obtained, indicating that it was free of lower nitrogen oxides. The purified N_2O_4 was stored over phosphorus pentoxide (Alfa).

Tetrabutyl ammonium nitrate and tetrabutyl ammonium nitrite were synthesized using modifications of the methods of Witschoke and coworkers[21] and Pocker and coworkers,[22] respectively.

Reaction Conditions. The reactions were carried out in a thermostated bath at 25.0 $\pm$ 0.5 ^{o}C unless specified

otherwise. All solutions were thoroughly purged with dry nitrogen. The reactions were carried out under dim illumination. Typically, 27 mg of fluoranthene dissolved in 0.9 mL of CCl_4 (15 mM) were allowed to react with 2.7 mL of a CCl_4 solution 18.4 mM in N_2O_4 (2.8 mM NO_2 in equilibrium with 17 mM N_2O_4) in a dark screw-capped vial with a minimum head space. Similar procedures were used with other solvents. When a third species was used, it was added to the solution containing the N_2O_4, before the mixing with the solution containing the fluoranthene. All reactions were carried out at least in duplicate and monitored by gas chromatography. The product distribution standard deviations, calculated by integration of the peak areas and correcting by their relative response factors to the flame ignition detector, were less than 10%.

Product distribution data represent the 0-20% fluoranthene conversion and no detectable change in product distribution was noticed as a function of the reaction progress.

Instrumentation. NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.13 MHz, using $CDCl_3$ as solvent and the residual $CHCl_3$ as internal standard (7.26 ppm). Samples were 10-15 mM in the nitro-PAH. COSY experiments were conducted using the 90^o-t_1-45^o-t_2 sequence, to avoid crowding around the diagonal,[23] employing Bruker software. For 2NF and 1,3DNF, a small

delay (D2=0.125 s) was introduced following the 90^{o} pulse to allow for polarization transfer via small couplings. Sine bell multiplication was done in both dimensions prior to Fourier transformation, and the spectra were symmetrized around the diagonal. Zero filling (one) was done only in the F2 dimension. For 2NF COSY 45, thirty two transients were collected for each 128 increments with a data set of 256 x 256. For 3NF COSY 45, sixteen transients were collected for each 512 increments with a data set of 1024 x 1024. Similarly, for 12DNF, sixty four transients were collected for each 128 increments with a data set of 256 x 256.

Quantitative analysis was done on a Varian 3700 gas chromatograph provided with a 55 m (0.25 mm I.D.) DB-17 J&W capillary column and a flame ionization detector.

Samples for NMR studies were purified by HPLC using hexane-methylene chloride mixtures on a Varian 5000 Liquid Chromatograph equipped with a 25 cm silica gel column (IBM).

The GC/MS analysis was conducted on a Hewlett-Packard 5890 GC instrument equipped with an HP 5970 mass-selective detector using a 20 m DB-17 J&W capillary column.

A one-hour photochemical experiment was conducted with a 200W Hg-Lamp in a homemade quartz cell provided with a teflon stopcock.

X-Ray Crystallography. Diffraction data were obtained from a yellow needle fragment of dimensions 0.18 x 0.24 x 0.40 mm on an Enraf-Nonius CAD4 diffractometer equipped with MoKα source (λ=0.71073 A) and a graphite monochromator. Crystal data are: $C_{16}H_8N_2O_4$, F.W.=292.3, monoclinic space group $P2_{1/n}$, a=4.968(3), b=13.815(2), c=18.444(3) A, σ=97.56(3)^o, V=1254.9(12) A^3, z=4, D_{calc}=1.547 g cm^{-3}, T=22 ^oC, μ(MoKα)=1.07 cm^{-1}. One quadrant of data having $1^o < \theta < 23^o$ was collected by ω - 2θ scans of variable rate 1.1-4.0 deg min^{-1}. Data reduction included correction for background, Lorentz, and polarization effects; no significant intensity decay ocurred during data collection. Of 1752 unique data, 1458 have positive net intensities and were used in the refinement.

The structure was solved by direct methods using MULTAN,[24] and refined by full-matrix least squares based on F with weights w= $\sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs.[25] Nonhydrogen atoms were treated anisotropically while H atoms were located by difference maps and refined isotropically. A secondary extinction coefficient refined to a value of $4.3(6)x10^{-7}$. Convergence was achieved with R=0.053 for 232 variables, maximum shift/esd < 0.01, and maximum residual density $0.18eA^{-3}$. Coordinates are listed in Table I.

RESULTS AND DISCUSSION

Product Identification. The GC-retention times of the nitrofluoranthenes follow the order 1NF < 7NF < 2NF < 3NF < 8NF < 1,3-dinitrofluoranthene (1,3DNF) < 1,2DNF under all conditions employed here. Mass spectra fragmentation patterns give characteristic M, M-30, and M-46 peaks, the last two, corresponding to loss of NO and NO_2, respectively.

The correct assignments of the ^{1}H-NMR resonances of nitro-PAH is important because the identification of their metabolites relies often on a comparison with the spectrum of the parent compound.[26] The identification of metabolites of mutagens is valuable because in some cases the metabolites display increased mutagenicity.[15,26-28] The major product of the reaction, 2NF, was identified by GC/MS and ^{1}H-NMR. Two previous reports of the ^{1}H-NMR spectrum are incomplete and partially incorrect.[3,12]

The members of the 2-spin, 3-spin and 4-spin subspectra of 2NF were identified by a COSY 45 experiment (Fig 1). As can be seen in Fig 2, ^{1}H-^{1}H nuclear Overhausser effect (NOE) difference spectroscopy provides unequivocal assignmments of the two downfield doublets. The combination of these two techniques also provides the assignment of H-4, H-5, H-6, H-7, and H-10. H-8 and H-9 can be assigned as tightly coupled partially superimposing multiplets between 7.42-7.50 ppm.

Atom	x	y	z	Atom	x	y	z
O1	1.0094(5)	0.1357(2)	0.5544(1)	C6	0.4569(6)	0.2379(2)	0.3113(1)
O2	0.6320(5)	0.2019(2)	0.5722(1)	C7	0.6466(6)	0.3167(2)	0.3000(1)
O3	1.4280(5)	0.4116(2)	0.5860(1)	C8	0.8063(6)	0.3319(2)	0.3675(1)
O4	1.1391(5)	0.3181(2)	0.6276(1)	C9	0.7353(6)	0.2671(2)	0.4213(1)
N1	0.8390(5)	0.1988(2)	0.5436(1)	C10	0.8820(6)	0.2732(2)	0.4890(1)
N2	1.2299(5)	0.3578(2)	0.5776(1)	C11	1.0886(6)	0.3446(2)	0.5032(1)
C1	0.2498(6)	0.1964(2)	0.2649(2)	C12	1.1534(6)	0.4056(2)	0.4501(2)
C2	0.0980(6)	0.1234(2)	0.2906(2)	C13	1.0134(6)	0.4001(2)	0.3787(2)
C3	0.1555(6)	0.0908(2)	0.3618(2)	C14	1.0614(6)	0.4553(2)	0.3169(2)
C4	0.3629(6)	0.1322(2)	0.4100(2)	C15	0.9098(6)	0.4396(2)	0.2513(2)
C5	0.5124(6)	0.2063(2)	0.3850(2)	C16	0.6973(6)	0.3708(2)	0.2417(2)

Table I. Atomic Coordinates for 1,2-Dinitrofluoranthene.

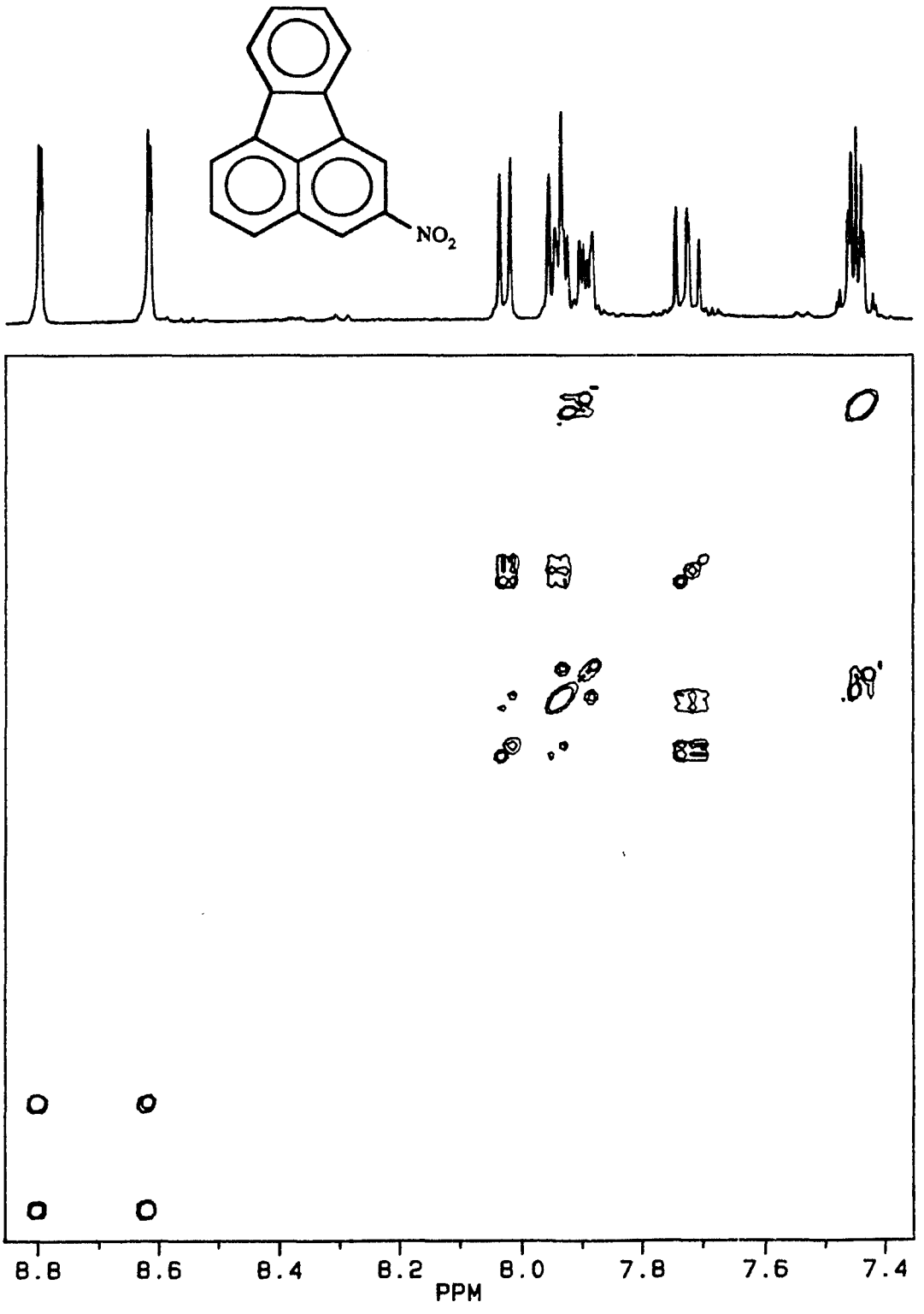


Fig. 1. 400 MHz ^{1}H-^{1}H COSY 45 of 2-Nitrofluoranthene.

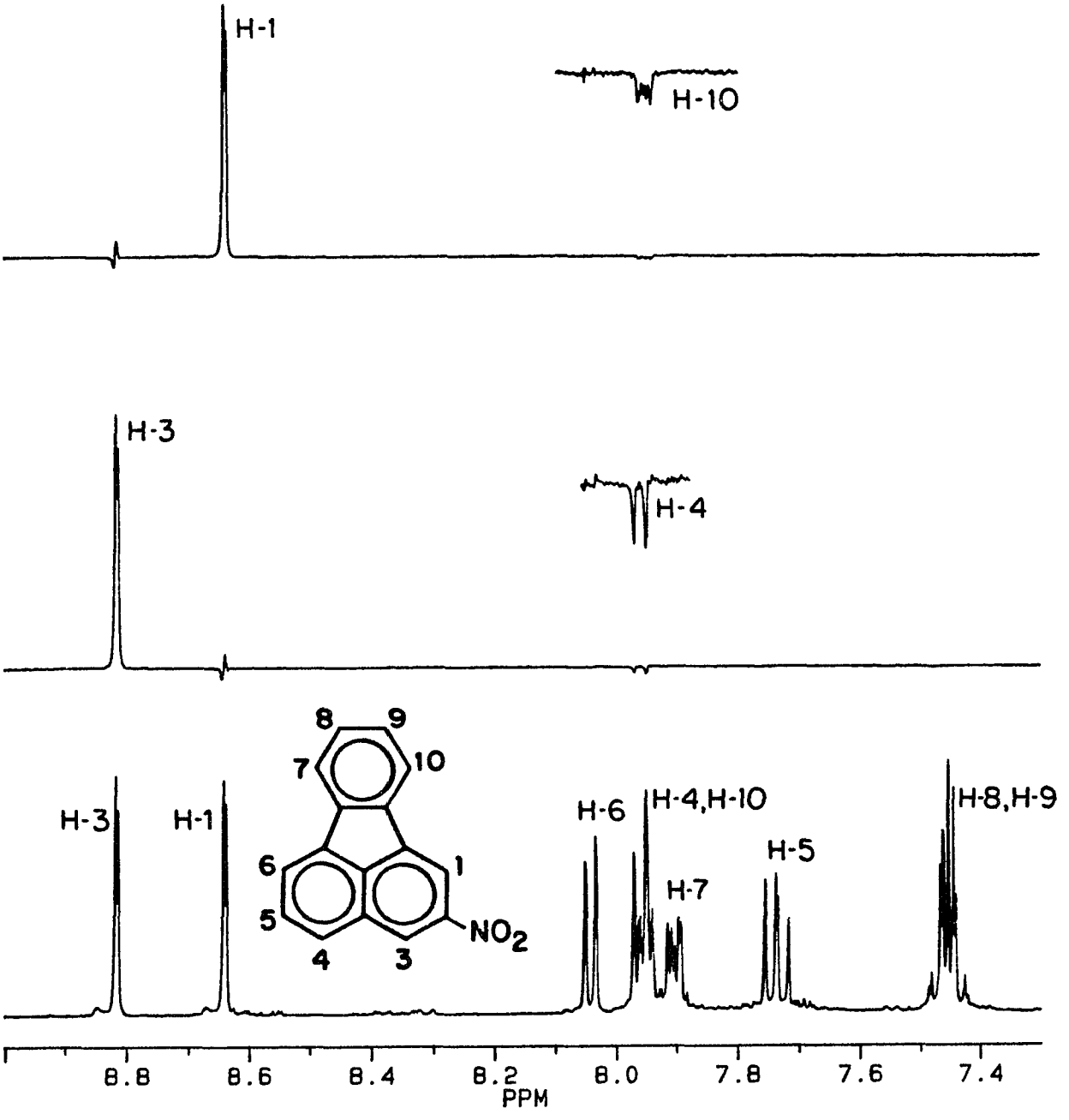


Fig. 2. NOE Difference Spectroscopy Experiments on 2-Nitrofluoranthene.

The other major mononitrofluoranthene, 3NF, was also identified by GC/MS and ^{1}H-NMR. As with 2NF, there are two very dissimilar reports of its ^{1}H-NMR spectrum.[3,29] Aromatic compounds may associate, and changes in chemical shifts may occur;[30] however, with the nitrofluoranthenes we have noticed only small changes (0.01-0.02 ppm) over a ten-fold range of concentrations. We therefore believe one of the reports of NMR parameters[29] actually is that of derivatized 3NF produced during manipulation. This report also finds 7NF to be unstable.[29] However, we find that all nitrofluoranthenes display exceptional thermal stability, although they are labile in light and their yellow solutions darken over a period of a few days when exposed to bright laboratory fluorescent light.

Our ^{1}H-NMR data of 3NF are consistent with those reported by Paputta-Peck and coworkers.[3] We determined the chemical shifts of H-6 (7.93 ppm) and H-1 (7.91 ppm) via the COSY 45 experiment shown in Fig 3. The chemical shifts of the pairs H-7 and H-10 (7.89 and 7.87 ppm) and of H-8 and H-9 (7.43-7.47 and 7.39-7.43 ppm) are interchangeable. The chemical shifts of the ^{1}H-NMR resonances of 8-NF and 1NF were assigned using the combined information obtained from NOE-difference spectroscopy and a COSY 45 experiment for each case. Similarly, the corresponding resonances of 7NF were assigned using of a COSY 45 experiment optimized for small

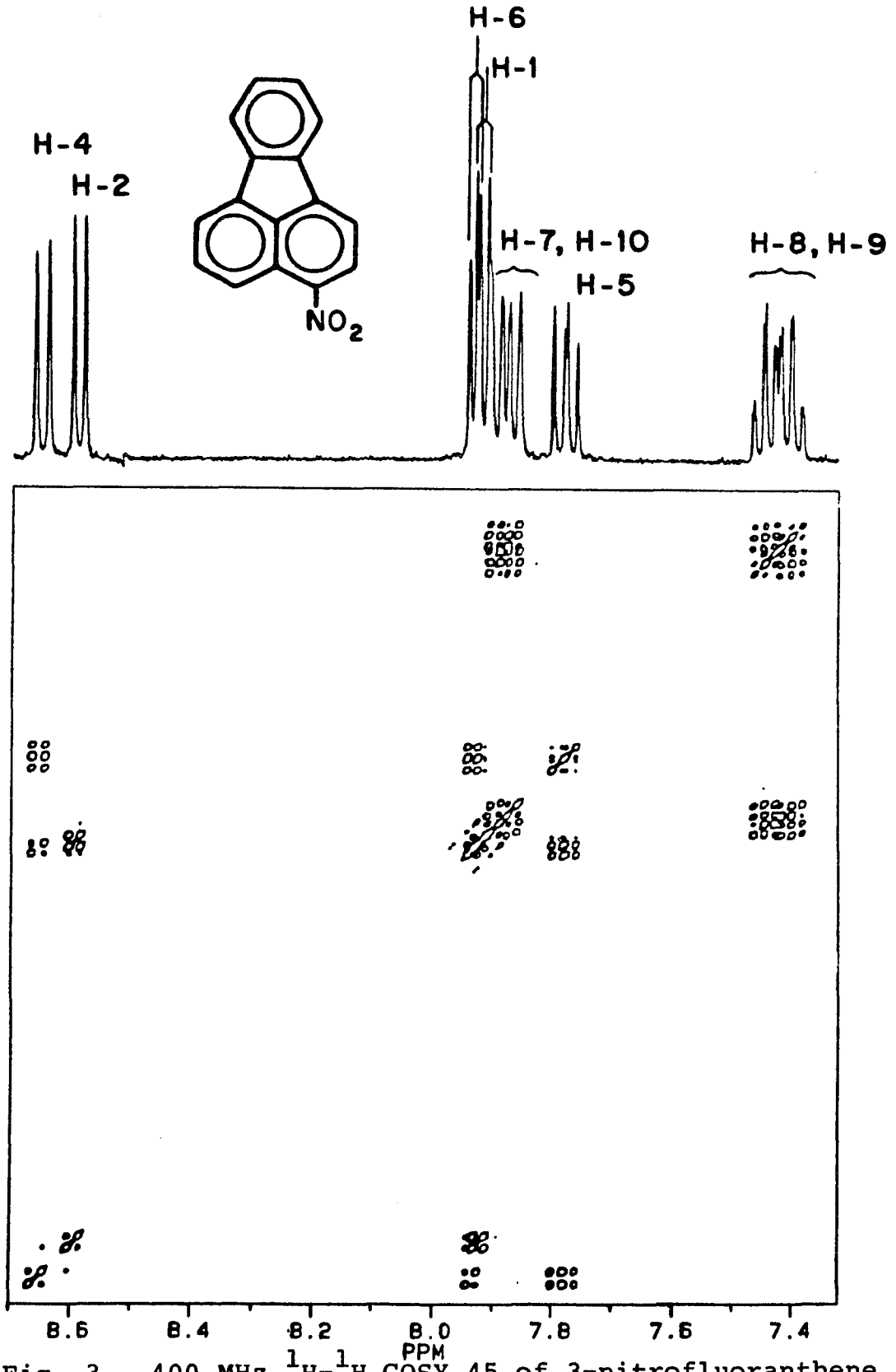


Fig. 3. 400 MHz ^{1}H-^{1}H COSY 45 of 3-nitrofluoranthene.

couplings.

The ^{1}H-NMR resonances of 12DNF were assigned by the same procedure used with 8NF and 1NF, revealing a discrepancy with a previous report.[12] The NMR experiments conducted on 1NF, 7NF, 8NF and 1,2DNF will be published elsewhere.[28]

1,3-Dinitrofluoranthene, a new dinitrofluoranthene, was identified by GC/MS and by ^{1}H-NMR. Irradiation of the downfield singlet did not result in any observable NOE on H-10 (contrasting with 2NF where moderately strong NOE (ca. 4%) is observed for a similar experiment) discarding the possibility of 2,3DNF as an alternative assignment. The ^{1}H-NMR resonances were assigned with the aid of the COSY 45 experiment shown in Fig 4. Its ^{1}H-NMR spectrum consists of a singlet, a three-spin and a four-spin subspectrum with farthest downfield members of the last two adjacent to the nitro groups. The chemical shifts of H-8 and H-9 were determined by a homodecoupling experiment experiment in which H-10 was irradiated, causing the collapse of the H-8 multiplet to almost a doublet (data not shown).

The ^{1}H-NMR parameters of the nitrofluoranthenes are summarized in Table II.

Chemistry of Nitrogenous Species Present in the Nitration System. Nitrogen dioxide is in rapid equilibrium with N_2O_4[31] and the equilibrium lies towards

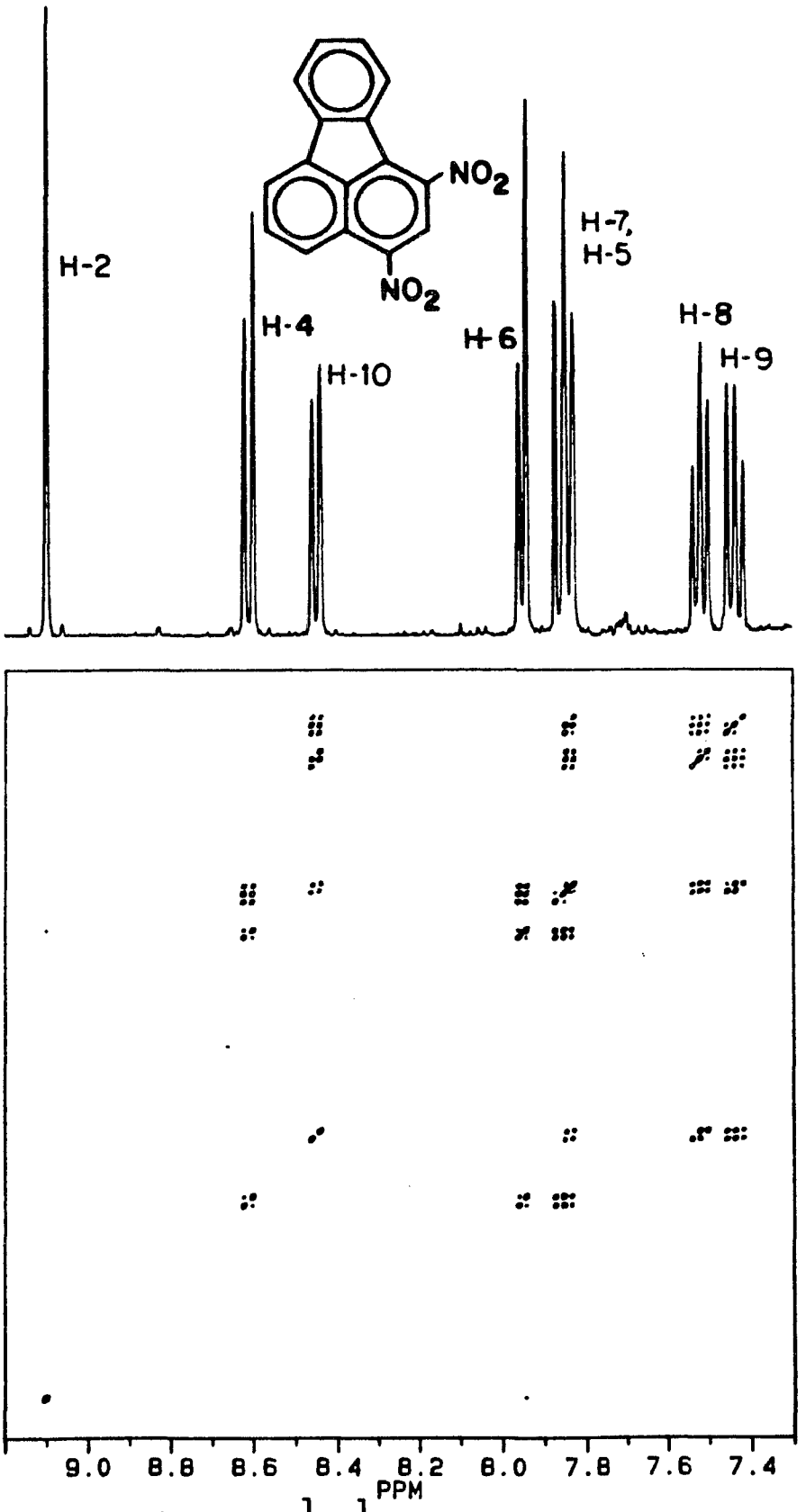


Fig. 4. 400 MHz ^{1}H-^{1}H COSY 45 of 1,3-dinitrofluoranthene.

	1NF[a]	2NF[a]	3NF[a]	7NF[a]	8NF[a]	1,2DNF[a]	1,3DNF[a]
H1	-----	8.64,d	7.91,d	8.08,d	8.11,d	-----	-----
H2	8.21,d	-----	8.58,d	7.72,d	7.75,dd	-----	9.10,s
H3	7.91,d	8.81,d	-----	7.99,d	8.01,d	8.67,s	-----
H4	7.83,d	7.96,d	8.65,d	8.03,d	7.98,d	7.96,d	8.62,br d
H5	7.72,dd	7.74,dd	7.78,dd	7.76,dd	7.75,dd	7.83,dd	7.86,dd
H6	7.95,d	8.04,d	7.93,d	8.68,d	8.09,d	8.09,d	7.96,br d
H7	7.89,br d	7.88-7.92,m	7.89,br d[b]	-----	8.76,dd	7.90,d	7.85,d
H8	7.46-7.50,m	7.42-7.50,m[c]	7.87,br d[b]	8.22,dd	-----	7.50-7.54,m	7.50-7.54,m
H9	7.41-7.45,m	7.42-7.50,m[c]	7.43-7.47,m[d]	7.54,dd	8.31,dd	7.41-7.45,m	7.42-7.46,m
H10	8.49,br d	7.93-7.97,m	7.39-7.43,m[d]	8.10,dd	8.03,dd	7.83,d	8.45,br d

Table II. ^{1}H-NMR Parameters of Nitrofluoranthenes. [a]Relevant coupling constants are summarized as follows: 1NF: J(2,3)=9Hz; J(4,5)=8Hz; J(5,6)=7Hz; J(7,8)=8Hz; J(9,10)=8Hz; 2NF: J(1,3)=2Hz; J(4,5)=8Hz; J(5,6)=7Hz; 3NF: J(1,2)=8Hz; J(4,5)=8Hz; J(5,6)=7Hz; J(7,8)=7Hz; J(9,10)=7Hz; 7NF: J(1,2)=8Hz; J(2,3)=8Hz; J(4,5)=8Hz; J(5,6)=7.5Hz; J(8,9)=7Hz; J(8,10)=1Hz; J(9,10)=8Hz; 8NF: J(1,2)=6.5Hz; J(2,3)=8Hz; J(4,5)=8Hz; J(5,6)=7Hz; J(7,9)=2Hz; J(7,10)=0.3Hz; J(9,10)=8Hz; 1,2DNF: J(4,5)=9Hz; J(5,6)=7Hz; J(7,8)=8Hz; J(9,10)=8Hz; 1,3DNF: J(4,5)=9Hz; J(5,6)=7Hz; J(7,8)=8Hz; J(9,10)=8Hz. [b]Interchangeable pair. [c]H8 and H9 are partially superimposing in 2NF. [d]Interchangeable pair.

the dimer[32,33] under the conditions used here. Nitrous acid, a by-product of the aromatization of the intermediates depicted in Scheme I, is unstable and rapidly decomposes at room temperature to NO, NO_2, N_2O_3, and water. Water, in turn hydrolyses N_2O_4 to HNO_3 and HONO. The result is a net accumulation of HNO_3 as the reaction proceeds, as can be seen by adding equations 1, 2 and 3.

$$2HONO \rightleftharpoons NO + NO_2 + H_2O \qquad (1)$$

$$2NO_2 \rightleftharpoons N_2O_4 \qquad (2)$$

$$N_2O_4 + H_2O \rightleftharpoons HONO + HONO_2 \qquad (3)$$

Sum: $$HONO + NO_2 \rightleftharpoons NO + HONO_2 \qquad (4)$$

As the solvent polarity increases, heterolytic equilibria, that produce NO^+ as a reactive species become increasingly dominant.[34] The nitrosonium ion has been found to play an important role in the electrochemical nitration of naphthalene by N_2O_4 in the polar aprotic solvent sulfolane.[34]

In the presence of oxygen, NO is oxidized to NO_2, equation 5.

$$NO + 1/2O_2 \longrightarrow NO_2 \qquad (5)$$

It can be seen by adding equations 4 and 5, as shown

in equation 6, that the presence of oxygen results in a net accumulation of $HONO_2$.

$$HONO + 1/2O_2 \longrightarrow HONO_2 \qquad (6)$$

The Effect of Selected Additives. Table III shows the effect various additives have in the product distribution of the reaction of 1 with NO_2/N_2O_4 in CCl_4. A small amount of HNO_3 does not interfere with the radical nitration because of the micelle-like characteristics of the dilute solutions of $HONO_2$[35] and the poor solvation of cationic intermediates in CCl_4.[14] The inertness of $HONO_2$ is evidenced by a product distribution independent of the extent of conversion (see Experimental Section) in the nitration of 1 with NO_2/N_2O_4 in CCl_4, and thus, independent of the increase in $HONO_2$ concentration as the reaction proceeds. Furthermore, when 6.6 mM $HONO_2$ is present initially, the formation of only 3% 8NF indicates the ionic contribution seems to be minimal. Similarly, yields are virtually unchanged when the reaction is run with an initial concentration of water of 30.9 mM. The product distribution obtained by using only anhydrous $HONO_2$ (0.17 M) as nitrating reagent gave very small amounts of 2NF (1%) and much larger amounts of 3NF (67%), 8NF (24%), 7NF (4%) and 1NF (3%). Therefore, nitration by $HONO_2$ occurs only at high concentrations and affords a

	%-distribution of products						
Additive	1NF	2NF	3NF	7NF	8NF	1,2DNF	1,3DNF
None	1	73	14	a	a	3	9
HNO_3 (6.6 mM)	1	53	30	a	3	5	9
HNO_3[b]	3	1	67	4	24	a	a
$NOBF_4$ (10 mM)	5	9	60	5	19	1	1
CH_3SO_3H (4.3 mM)	2	34	43	2	10	3	7
Oxygen[c]	2	59	19	1	7	8	4
$TBANO_2$[d] (1.0 mM)	1	60	12	a	a	13	15
$TBANO_3$[e] (1.3 mM)	1	58	12	a	a	13	17
DTBP[f] (1.3 mM)	1	58	14	a	a	13	14
H_2O (30.9 mM)	1	67	18	a	a	5	10
$CBrCl_3$ (2.15 M)	2	72	10	2	1	4	12

Table III. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO_2 in CCl_4 as a Function of Selected Added Species. [a]Less than 0.5%. [b]HNO_3 0.17M. No NO_2 was added. [c]Reaction carried out in O_2-saturated CCl_4. [d]Tetrabutylammonium nitrite. [e]Tetrabutylammonium nitrate. [f]2,6-Di-tert-butylpyridine.

very different product distribution.

The effect of acidity was also investigated. When the reaction was run in the presence of 4.3 mM CH_3SO_3H, the formation of substantial amounts of 8NF (10%) and much smaller amounts of 2NF (34%) was observed. An even more pronounced effect was observed when the reaction was carried out in the presence of a small amount of $NOBF_4$ (ca. 10 mM).

Tetrabutylammonium nitrite ($TBANO_2$), tetrabutylammonium nitrate ($TBANO_3$) and 2,6-di-tert-butylpyridine (DTBP) cause the formation of moderately larger amounts of dinitrofluoranthenes and lower the 2NF/3NF ratio without the concomitant formation of 8NF.

The presence of oxygen increases the 1,2DNF/1,3DNF and 3NF/2NF ratios and induces the formation of 8NF (7%), 1NF (2%) and 7NF (1%).

The effect of light was also investigated. Irradiation with a 200 W mercury lamp for one hour afforded a complex mixture of chlorofluoranthenes and nitrochlorofluoranthenes.

Temperature Effects. The effects of temperature on the reaction are shown in Table IV. At lower temperatures, 1NF, 3NF, 7NF, and 8NF become increasingly predominant. In contrast, the dinitrofluoranthenes are reduced to trace levels.

The Effect of Solvent Polarity. Contrary to our

	%-distribution of products						
Temp. (°C)	1NF	2NF	3NF	7NF	8NF	1,2DNF	1,3DNF
40	2	65	13	a	1	10	10
25	1	73	14	a	a	3	9
10	4	54	22	3	5	7	6
-13	4	30	51	4	12	a	a

Table IV. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO_2 in CCl_4 as a Function of Temperature. [a]Less than 0.5%.

results obtained with CCl_4, the reaction in CH_2Cl_2 is strikingly sensitive to trace amounts of water, as shown in Table V. In dry CH_2Cl_2, and at low conversions, the reaction is predominantly radical, although there are substantial amounts of ionic products (e.g. 10% 8NF). When the reaction is run in the presence of 30 mM water, the ionic pathway predominates, producing larger amounts of 8NF (19%) and 3NF (63%). The addition of water reduces the yields of dinitrofluoranthenes. On the other hand, the ionic products are diminished when the reaction is run in the presence of 12.4 mM DTBP.

Mechanistic Considerations. In CCl_4, the nitration of 1 by NO_2 should be regarded as occurring exclusively via a mechanism involving free radicals. The radical reaction pathway being characterized by the formation of 2NF as the major product and by anomalously large amounts of unusual dinitration products even at low conversions. We have previously interpreted the formation of these products as arising via a free radical mechanism involving multiple addition-elimination steps.[14] The formation of 2NF is favored over that of 3NF apparently due to the peri interaction of the nitro-group in the latter case. The two dinitrofluoranthene isomers formed present disubstitution in the same ring of the naphthalene-like moiety. In contrast to the behavior displayed with the mononitrofluoranthenes, thermodynamic control for the

	%-distribution of products						
Additive	1NF	2NF	3NF	7NF	8NF	1,2DNF	1,3DNF
None	2	32	43	1	10	5	6
H_2O (30.9 mM)	2	9	63	3	19	2	2
DTBP[a] (12.4 mM)	b	35	46	a	5	7	8

Table V. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO_2 in CH_2Cl_2 as a Function of Selected Added Species. [a]2,6-Di-tert-butylpyridine. [b]Less than 0.5%.

formation of the dinitrofluoranthenes does not seem to be operative due to the higher instability of the tetrahydrotetranitrofluoranthene intermediate. The 1,3DNF/1,2DNF ratio is only 3, despite of the strong steric repulsion present in 1,2DNF as evidenced in the ORTEP drawing of its crystal structure (Fig 5).

An ionic pathway, which is catalyzed by CH_3SO_3H and more efficiently by $NOBF_4$, is characterized by a higher yield of 8NF and a product distribution in closer agreement with that of the cationic σ-complex theoretical prediction. When $HONO_2$ is used as the only nitrating species, only a very small amount of 2NF (1%) is formed together with major products consistent with an ionic electrophilic reaction pathway. Therefore, nitration by the by-product $HONO_2$ in CCl_4 is not an important reaction pathway.

Tetrabutylammonium nitrite, $TBANO_3$ and DTBP appear to exert their effects at the elimination steps in Scheme I that lead to aromatization. These nucleophiles increase the dinitrofluoranthene/mononitrofluoranthene ratio, slightly lower the 2NF/3NF ratio, and do not cause formation of 8NF. These nucleophiles further prove that NO^+ and NO_2^+ in CCl_4 are not involved. The reaction pathways involving NO^+ and $NO2^+$ would be blocked by mass action by the addition of $TBANO_2$ and $TBANO_3$ (as can be seen in equations 7 and 8); however, the same products are

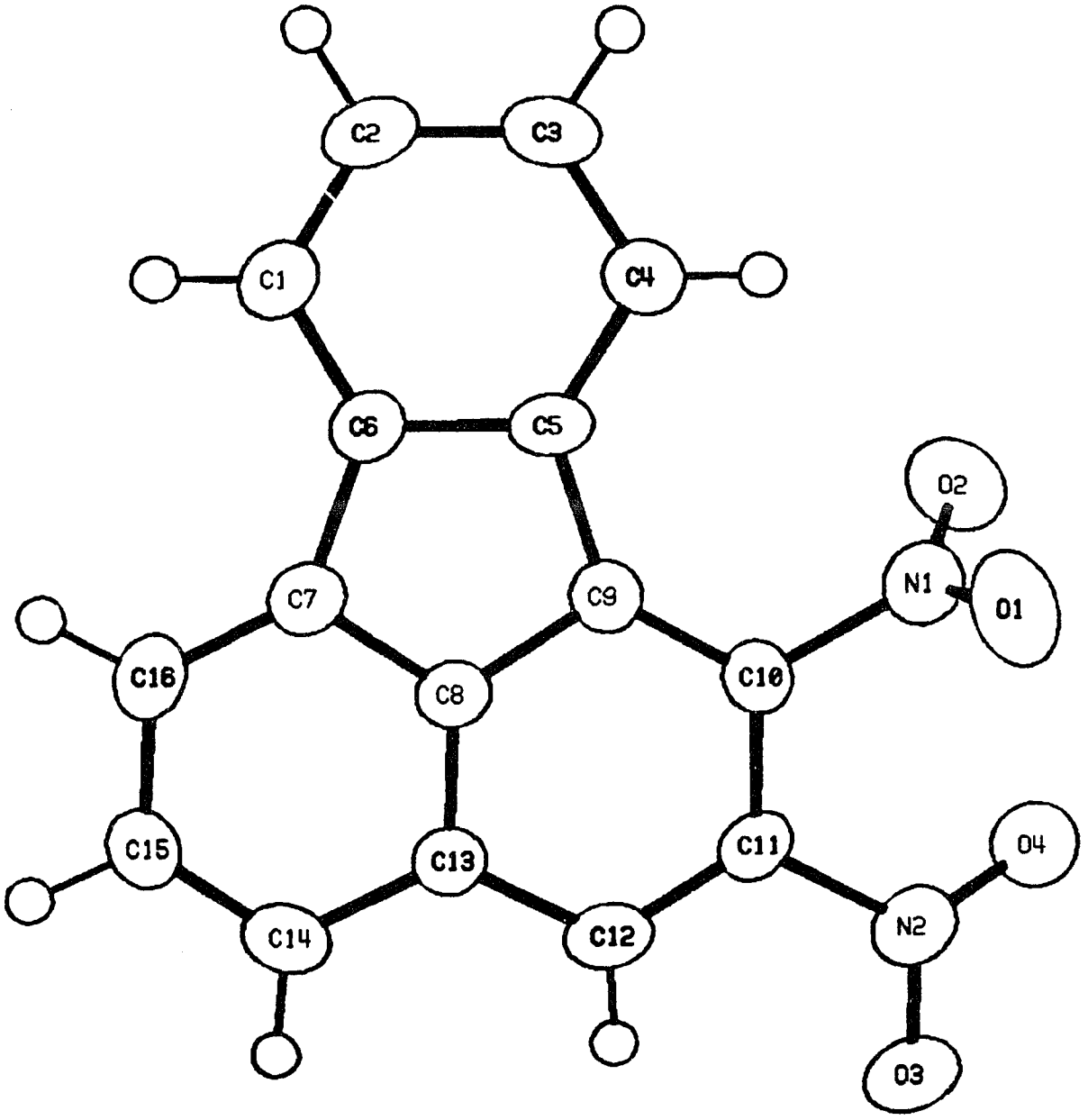


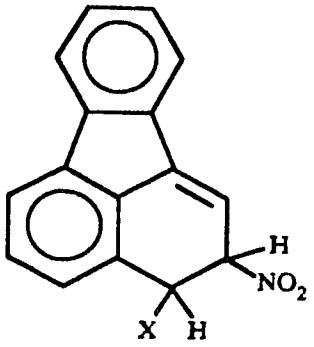
Fig. 5. ORTEP-drawing of the X-Ray structure of 1,2-dinitrofluoranthene showing the spatial orientation of the nitro-groups. Nitro-group$_1$ and nitro-group$_2$ form angles of 73.2° and 11.2° with the plane containing the carbon skeleton, respectively. The nitro-groups are at an angle of 73.4° with respect to each other. The dihedral angles described above are those formed by the least-squares planes containing the appropriate atoms. The carbon-atom to which the nitro-group is attached was also included for the calculation of the corresponding least-squares plane.

observed with or without $TBANO_2$ or $TBANO_3$. The

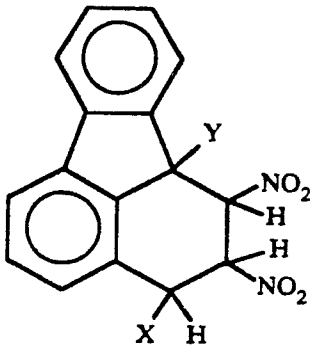
$$NO^+ + NO_3^- \rightleftharpoons N_2O_4 \quad (7)$$

$$NO_2^+ + NO_2^- \rightleftharpoons N_2O_4 \quad (8)$$

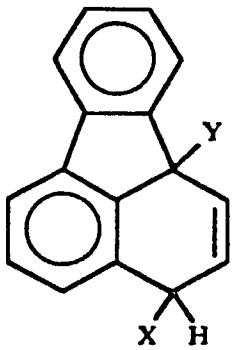
increase in the dinitrofluoranthene/mononitrofluoranthene probably arises from a competitive reaction pathway of nucleophilic addition of NO_2^- or NO_3^- to the double bond of adduct I ($X=NO_2$). The resulting anion could be oxidized by NO_2 to the corresponding radical that will react by coupling with an NO_2 yielding adduct II ($X=NO_2$; $Y=NO_2$ or NO_3). Adduct II can subsequently eliminate HONO and $HONO_2$ to yield 1,2DNF and 1,3DNF. Alternatively, NO_2^- or NO_3^- could react with adduct I in a SN_2' fashion to yield adduct III ($Y=NO_2$ or NO_3). Adduct III can then react with two equivalents of NO_2 to yield adduct II ($X=NO_2$; $Y=NO_2$, or NO_3) which can rearomatize to yield 1,2DNF and 1,3DNF.



I



II



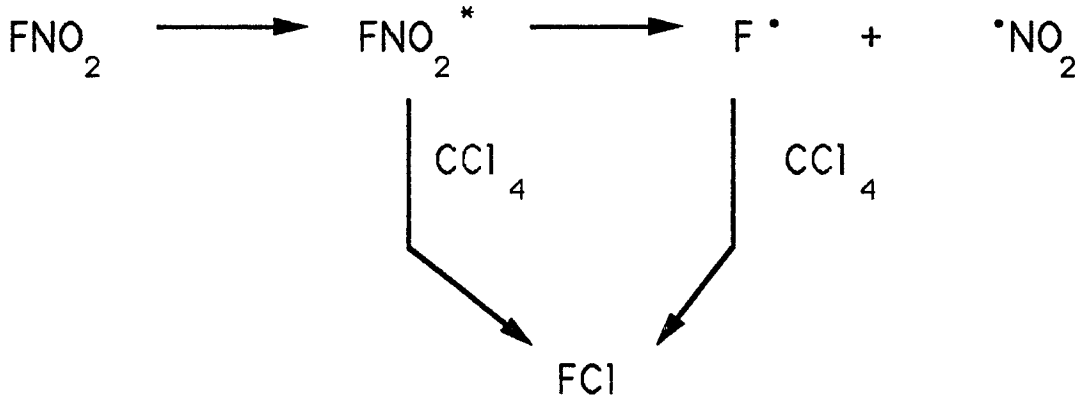
III

Radical coupling between the intermediate radicals and NO_2 is faster than bromine-atom abstraction from $BrCCl_3$ since neither could bromofluoranthenes be detected nor was there a change in product distribution when the reaction was carried out in the presence of 2.15 M $BrCCl_3$ (Table III).

Irradiation appears to induce homolytic dissociation of the mono- and dinitrofluoranthenes to the corresponding fluoranthenyl radicals which in turn can abstract a chlorine-atom from the solvent and produce the chlorofluoranthenes (Scheme II). Alternatively, a diradicaloid excited triplet-state may abstract a chlorine-atom from the solvent, and, ultimately lead to the observed products.[36] Thus, the effect of light is complicated by the promotion of chlorine-atom abstraction from the solvent by the thermal nitration products.

The effect of oxygen deserves special attention. Zielinska and collaborators[12] observed the formation of 1,2DNF (in addition to 2NF) when 1 was allowed to react with N_2O_5 in CCl_4. It is therefore possible that oxygen reacts with NO_2 to form small amounts of more highly oxygenated species (that are more reactive than NO_2) like NO_3 and/or NO_4.[37] Elimination of the more highly oxygenated nitrogenous acids from adducts I and II (where X is a highly oxygenated nitrogenous species) appears to be thermodynamically favorable; thus, the preference for

Scheme II



F = fluoranthene or nitrofluoranthene

the formation of 1,2DNF over 1,3DNF would be explained. For example, the gas phase heat of formation of nitric acid is 13.3 Kcal/mol more exothermic than that of nitrous acid.[38] Thus, rearomatization of adduct II (where X is a highly oxygenated nitrogenous substituent) would lead to 1,2DNF. Rearomatization of adduct I (where X is a highly oxygenated nitrogenous species) would lead to the formation of larger amounts of 2NF, in apparent contradiction with the experimental results. We believe, however, that the larger amounts of 3NF observed in the presence of oxygen are formed by a concomitant ionic reaction pathway brought about by the oxidation of HONO to $HONO_2$. The observation of larger amounts of other nitrofluoranthenes characteristic of ionic nitration (e.g. 8NF, 7NF, and 1NF) is consistent with this explanation.

At lower temperatures, the ionic component of the reaction mechanism becomes increasingly predominant. The radical process is expected to show a stronger temperature dependance because the activation energy for radical processes is usually larger than that of their ionic counterparts. Other factors may also contribute to the predominance of the ionic rection pathway at low temperatures: (1) the shift of the NO_2/N_2O_4 equilibrium towards the less reactive dimer N_2O_4 as the temperature is lowered, thus, slowing the radical pathway down, and (2) the preference for ion pairs like $NO^+NO_3^-$ and/or $NO_2^+NO_2^-$

at lower temperatures which would be expected to promote ionic nitration, as we observe experimentally. A temperature-dependent product distribution also was observed by Zielinska and collaborators[12] for the reaction of N_2O_5 with 1.

A product distribution in closer agreement with the cationic σ-complex is obtained in solvents more polar than CCl_4. The attacking electrophile does not appear to be the nitronium ion because the reaction rates depend on the PAH[39], while the nitronium ion is known to react at a diffusion-controlled rate with the same set of PAH. It can be observed that there is substantial contribution of both the ionic and the radical reactions in carefully dried CH_2Cl_2 at low conversions. The addition of water promotes the ionic pathway by disproportionating the N_2O_4 to HONO and $HONO_2$, while the addition of DTBP quenches the HONO and $HONO_2$ that are formed as the reaction proceeds and, therefore, prevents the formation of NO^+,[33,34] a very efficient catalyst of the ionic reaction (Table V). Thus, DTBP is an inhibitor of the ionic reaction.

In solvents of dielectric constant higher than CH_2Cl_2, only small amounts of 2NF are formed, as can be seen in Table VI. This result is consistent with a better solvation of cationic intermediates relative to that of the radical intermediates as the solvent dielectric constant is increased. It is also noticeable that emerald

	%-distribution of products[a]				
Solvent	1NF	2NF	3NF	7NF	8NF
THF	4	9	57	5	25
CH_3CN	4	5	67	5	19
CH_3NO_2	4	1	72	4	22

Table VI. Distribution of Nitro- and Dinitrofluoranthenes Formed in the Nitration of Fluoranthene with NO_2 as a Function of the Solvent. [a]1,2DNF and 1,3DNF are present in less than 0.5%.

green charge-transfer complexes of these solvents with N_2O_4 are formed.[40] These complexes may play a role in the formation of the ultimate electrophile by causing extensive polarization of N_2O_4.

We believe that the use of 1 as a mechanistic probe can be expanded to other aromatic substitution reactions in which changes in solvent polarity and/or temperature may make ionic and radical pathways competitive. For example, Nonhebel and his collaborators have studied the reaction of substituted anthracenes in CCl_4 with Cu(II) halides,[41-43] and conclude that the reaction involves halogen-atom addition[41] (or hydrogen-atom abstraction from a 9-methyl-substituted position[42]), while it proceeds via a nonbonded electron-transfer mechanism in methanol.[43] In addition, our proposed multiple-step addition-elimination mechanism for 1 also offers a plausible alternative explanation to certain anomalies in the nitration of pyrene,[44,45] in which unusually large amounts of dinitropyrenes, including the unexpected 1,3-dinitropyrene, are formed.

The possibility that the formation of charge-transfer complexes is the rate-determining step in the reaction of PAH with NO_2 is currently under investigation.[39,46] The formation of charge-transfer complexes may give further insights to a more general mechanism since the relative rates of several PAH with NO_2

in CH_2Cl_2 were found to correlate best with their half-wave oxidation potentials,[39] which in turn, may parallel stability of their charge transfer-complexes.

Although the synthetic applications of the nitration of PAH with NO_2 in organic solvents are attractive,[10,39,47] special attention should be given to the choice and water content of the solvents, drying of the NO_2, temperature, and catalysts. As we have demonstrated, the reaction mechanism is highly dependent upon experimental conditions.

Toxicological Implications. Fluoranthene is one of the most abundant PAH in environmental samples.[48] The reaction of 1 with NO_2 is slower than that with N_2O_5;[12,14] nevertheless, the reaction with NO_2 might be the most important contributor to the formation of 2NF due to the relatively higher concentrations of NO_2 in urban atmospheres.[49] There currently is evidence for a substantial contribution from a non-ionic reaction pathway (apparently gas phase atmospheric reactions) to the total nitro-PAH in the urban environment.[4,8,9,13,14] The distribution of nitro-PAH obtained upon nitration with NO_2 under free radical conditions (e.g. in solvents of low dielectric constant) may model the atmospheric (gas phase) reaction. For example, 2-nitrofluoranthene is one of the most important nitro-PAH in ambient polluted air,[50] and, as we have found, is the major product of the homolytic

nitration of 1 with NO_2. In contrast, 2-nitrofluoranthene is the only isomer not detected under nitrations mediated by the nitronium-ion or a carrier thereof. Thus, a number of similarities between the distribution of nitro-PAH ambient air pollutants and the distribution of nitro-PAH obtained by free radical nitration with NO_2 are now evident.[51] The nitration of 1 with NO_2 under free radical conditions also leads to the facile formation of highly mutagenic dinitrofluoranthenes.[15,28] Although there are currently no data indicating that dinitrofluoranthenes are atmospheric pollutants, they display GC retention times similar to those of the more studied dinitropyrenes[45,52] and also have the same molecular weight and similar MS fragmentation patterns. Thus, what has been identified as dinitropyrenes by gas chromatography may actually reflect the sum of dinitropyrenes and dinitrofluoranthenes.

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Supplementary Material Available: X-ray crystallographic data for 1,2-dinitrofluoranthene:

complete tables of bond distances and angles, coordinates for hydrogen atoms, and anisotropic thermal parameters (5 pages); listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Chapter II. Supplementary Material.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N1	1.213(3)	C7	C16	1.360(4)
O2	N1	1.217(4)	C8	C9	1.414(4)
O3	N2	1.227(3)	C8	C13	1.390(4)
O4	N2	1.211(3)	C9	C10	1.363(4)
C1	C2	1.381(4)	C10	C11	1.423(4)
C1	C6	1.374(4)	C10	N1	1.474(4)
C2	C3	1.381(4)	C11	C12	1.363(4)
C3	C4	1.392(4)	C11	N2	1.467(4)
C4	C5	1.379(4)	C12	C13	1.407(4)
C5	C6	1.420(4)	C13	C14	1.418(4)
C5	C9	1.477(4)	C14	C15	1.355(4)
C6	C7	1.473(4)	C15	C16	1.414(4)
C7	C8	1.401(4)			

Table I. Bond Distances for 1,2-Dinitrofluoranthene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	C6	119.2(3)	C9	C10	C11	119.8(3)
C1	C2	C3	120.7(3)	C9	C10	N1	118.3(2)
C2	C3	C4	121.1(3)	C11	C10	N1	121.6(2)
C3	C4	C5	118.6(3)	C10	C11	C12	121.9(2)
C4	C5	C6	120.1(2)	C10	C11	N2	120.2(2)
C4	C5	C9	132.5(3)	C12	C11	N2	117.8(3)
C6	C5	C9	107.4(2)	C11	C12	C13	120.3(3)
C1	C6	C5	120.2(3)	C8	C13	C12	116.1(3)
C1	C6	C7	131.3(3)	C8	C13	C14	116.4(2)
C5	C6	C7	108.4(2)	C12	C13	C14	127.5(3)
C6	C7	C8	106.4(2)	C13	C14	C15	120.0(3)
C6	C7	C16	135.0(3)	C14	C15	C16	122.5(3)
C8	C7	C16	118.6(3)	C7	C16	C15	118.9(3)
C7	C8	C9	111.3(2)	O1	N1	O2	124.5(3)
C7	C8	C13	123.7(3)	O1	N1	C10	116.9(3)
C9	C8	C13	124.9(2)	O2	N1	C10	118.5(2)
C5	C9	C8	106.5(2)	O3	N2	O4	123.4(2)
C5	C9	C10	136.7(3)	O3	N2	C11	118.1(2)
C8	C9	C10	116.8(3)	O4	N2	C11	118.4(2)

Table II. Bond Angles for 1,2-Dinitrofluoranthene.

Atom	x	y	z	Biso	Atom	x	y	z	Biso
H1	0.214(5)	0.216(2)	0.215(1)	2.9(6)	H12	1.278(5)	0.455(2)	0.464(1)	3.2(6)
H2	-0.044(5)	0.094(2)	0.258(1)	4.1(7)	H14	1.200(5)	0.506(2)	0.322(1)	2.6(6)
H3	0.057(5)	0.038(2)	0.381(1)	3.0(6)	H15	0.943(5)	0.477(2)	0.209(1)	4.0(7)
H4	0.399(4)	0.110(2)	0.457(1)	1.8(5)	H16	0.604(5)	0.362(2)	0.193(1)	2.8(6)

Table III. Coordinates and Thermal Parameters for Hydrogen Atoms for 1,2-Dinitrofluoranthene.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1	H1	0.94(2)	C12	H12	0.93(2)
C2	H2	0.96(2)	C14	H14	0.98(2)
C3	H3	0.97(2)	C15	H15	0.97(3)
C4	H4	0.91(2)	C16	H16	0.97(2)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	H1	120(1)	C11	C12	H12	118(1)
C6	C1	H1	121(1)	C13	C12	H12	122(1)
C1	C2	H2	119(2)	C13	C14	H14	120(1)
C3	C2	H2	120(2)	C15	C14	H14	120(1)
C2	C3	H3	122(1)	C14	C15	H15	120(1)
C4	C3	H3	117(1)	C16	C15	H15	117(1)
C3	C4	H4	120(1)	C7	C16	H16	123(1)
C5	C4	H4	121(1)	C15	C16	H16	118(1)

Table IV. Distances and Angles Involving Hydrogen Atoms in 1,2-Dinitrofluoranthene.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
O1	5.8(1)	4.7(1)	5.0(1)	1.4(1)	1.4(1)	1.6(1)	5.10(6)
O2	3.9(1)	7.4(1)	4.7(1)	-0.5(1)	1.83(9)	1.1(1)	5.22(6)
O3	5.1(1)	6.0(1)	4.4(1)	-2.6(1)	-1.3(1)	0.1(1)	5.33(6)
O4	5.2(1)	6.7(1)	2.7(1)	-1.7(1)	0.32(9)	-0.1(1)	4.89(6)
C1	2.8(2)	3.4(1)	2.6(1)	0.2(1)	0.1(1)	-0.4(1)	2.94(7)
C2	2.5(2)	3.6(1)	3.7(1)	-0.3(1)	0.1(1)	-1.0(1)	3.31(8)
C3	3.1(2)	3.0(1)	4.3(1)	-0.6(1)	1.0(1)	-0.4(1)	3.43(8)
C4	2.9(2)	3.3(1)	3.0(1)	-0.2(1)	0.6(1)	0.1(1)	3.07(8)
C5	1.8(1)	2.4(1)	3.2(1)	-0.0(1)	0.5(1)	-0.4(1)	2.44(7)
C6	2.2(1)	2.6(1)	2.4(1)	0.3(1)	0.3(1)	-0.3(1)	2.40(7)
C7	1.9(1)	2.7(1)	2.9(1)	0.4(1)	0.3(1)	-0.1(1)	2.53(7)
C8	1.9(1)	2.5(1)	2.6(1)	0.2(1)	0.5(1)	-0.3(1)	2.32(7)
C9	2.2(1)	2.7(1)	2.3(1)	0.3(1)	0.7(1)	-0.0(1)	2.36(7)
C10	2.6(2)	2.6(1)	2.3(1)	0.2(1)	0.5(1)	0.1(1)	2.50(7)
C11	2.6(2)	3.0(1)	2.3(1)	-0.1(1)	-0.2(1)	-0.4(1)	2.69(7)
C12	2.4(2)	2.8(1)	3.7(1)	-0.3(1)	0.2(1)	-0.4(1)	2.99(7)
C13	2.1(1)	2.5(1)	2.8(1)	0.2(1)	0.3(1)	-0.0(1)	2.46(7)
C14	2.8(2)	2.8(1)	4.0(1)	-0.3(1)	0.7(1)	0.2(1)	3.16(8)
C15	3.3(2)	3.4(1)	3.1(1)	-0.0(1)	0.4(1)	0.9(1)	3.29(8)
C16	3.2(2)	3.5(1)	2.5(1)	0.5(1)	0.0(1)	0.1(1)	3.07(7)
N1	3.7(1)	4.0(1)	2.7(1)	-0.3(1)	0.2(1)	-0.0(1)	3.49(6)
N2	3.4(1)	3.6(1)	3.3(1)	-0.1(1)	-0.2(1)	-0.3(1)	3.51(6)

Table V. Anisotropic Thermal Parameters for 1,2-Dinitrofluoranthene.

CHAPTER III. THE REACTION OF ANTHRACENE WITH NITROGEN DIOXIDE REVISITED

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ABSTRACT

The nitration of polycyclic aromatic hydrocarbons (PAH) by nitrogen dioxide has environmental importance because of the highly mutagenic properties of many nitro-PAH. The mechanisms of the reactions of PAH with NO_2 have been a matter of debate, and a variety of possible intermediates has been proposed. We find that the primary products of the reaction of anthracene (A) with nitrogen dioxide are cis- and trans-9,10-dinitro-9,10-dihydroanthracene, identified by NMR and single-crystal X-ray analysis. The chemical literature contains conflicting product analyses for this reaction, and the discrepancies are rationalized in terms of the thermal and chemical lability of these primary products. The formation of cis- and trans-9,10-dinitro-9,10-dihydroanthracene is rationalized in terms of a radical reaction of A with NO_2, rather than in terms of an electrophilic reaction mechanism. Analysis of the reaction kinetics reveals the formation of an intermediate that is apparently a charge-transfer complex, between A and one molecule of nitrogen dioxide. This intermediate preceeds the formation of the 9-nitro-9-hydroanthryl radical depicted in Scheme II because the coupling of bulkier hydroanthryl radicals and NO_2 has been previously found to approach diffusion control. The

logarithm of the rates of reactions of PAH with NO_2 correlate well with the half-wave oxidation potential of the PAH. Because the stability of the PAH cation-radicals may parallel the stability of their corresponding charge-transfer complexes, the log rate vs. E_{ox} correlation suggests that charge-transfer intermediates are formed in a rate-determining step in PAH/NO_2 reactions in nonparticipating solvents.

The study of the reaction of nitrogen dioxide with anthracene (A) can be traced back to the year 1880, when Lieberman and Lindeman suggested 9-nitro-10-nitrito-9,10-dihydroanthracene is the primary product when A in glacial acetic acid was allowed to react with NO_2.[2] Since Lieberman and Lindeman's first report, a series of other articles have provided conflicting results. Almost simultaneously and under similar conditions, Leeds isolated only anthraquinone (AQ).[3] Twenty-one years later, Meisenheimer proposed that 9,10-dinitro-9,10-dihydroanthracene (DDA) is the primary product of the reaction of A with NO_2 in chloroform.[4] Meisenheimer also noticed the ease with which DDA lead to 9-nitroanthracene (9NA) by elimination of the elements of nitrous acid. In 1924, Bass and Johnson[5] isolated only AQ under conditions similar to those of Meisenheimer. Meisenheimer's DDA was admitted by Barnett,[6] who recognized that it could exist in cis and trans forms, by Battegay[7], by Monti and coworkers[8] and by Sosnovsky;[9] however, the authors were unable to further characterize the adducts proposed by Meisenheimer. In 1938, Topchiev and his collaborators,[10] reported the formation of 9,10-dinitroanthracene in 80% yield for the reaction of A with NO_2 in chloroform. In 1963, Dufraisse and coworkers,[11] using A suspended in benzene or ether, were able to isolate two isomers which showed IR absorptions consistent with addition of NO_2 to

the 9 and 10 positions. In chloroform, however, they obtained only 9-nitro-10-nitrato-9,10-dihydroanthracene, apparently due to participation of ambient oxygen in their reaction system. Dufraisse[11] also provided the first spectroscopic support for the identification of the isomers of DDA (IR) and clarified reports of conflicting melting points and structures.[2-4,10] Recently, Eberson and Radner, reported a mixture of 9NA (93-95%) and AQ (5-7%) for the reaction of A with NO_2 in methylene chloride.[12,13] The stereochemistry and conformation of cis- and trans-DDA have not been reported.

We report herein a high-yield, one-pot method for the synthesis of the isomers of DDA. We also report the assignment of stereochemistry, ^1H and ^{13}C NMR-resonances in solution, and, the single-crystal X-ray analysis for cis- and trans-DDA. The mechanistic implications of these relatively labile compounds on the reaction of A with NO_2 in CCl_4, $CHCl_3$, and CH_2Cl_2 are discussed in terms of a radical reaction and as proof against an ionic electrophilic mechanism. In addition, stopped-flow kinetics evidence for a first intermediate of the charge-transfer type has been obtained. A charge-transfer intermediate is consistent with the linear relationship previously found between the logarithm of relative rates of reaction of several PAH and their half-wave oxidation potentials.[14]

Recently, we proposed multiple-addition intermediates for the radical reactions of fluoranthene[15,16] and naphthalene[17] with NO_2 on the basis of changes in product distributions as function of solvent, temperature and selected added species. The intermediates in the reactions of fluoranthene and naphthalene with NO_2 are unstable and rapidly lose nitrous acid to aromatize. With A however, a minimal aromatization energy for the central ring warrants a higher thermal stability of its addition products (cis- and trans-DDA) and supports the viability of our proposed fluoranthene and naphthalene adducts. A common pattern for the reaction of PAH with NO_2, in the abscence of acid catalysis, seems to have emerged.

EXPERIMENTAL SECTION

Reagents and Materials. Anthracene (Baker, 99.9+%) was used without further purification. Nitrogen dioxide was purchased from Matheson, distilled, and dried over P_2O_5 until a white solid was obtained upon freezing the distillate, in order to free the distillate from lower oxides of nitrogen. CCl_4 (Mallinckrodt Analytical Reagent) was dried over molecular sieves. CH_2Cl_2 (Mallincrodt ChromAr HPLC) was dried over sodium sulfate, distilled, and stored over molecular sieves. $CHCl_3$ (Baker Analized Reagent) was repeatedly washed with water, dried over $CaCl_2$, distilled and kept over $CaCl_2$. CD_2Cl_2 and

$CDCl_3$ were obtained from Aldrich Chemical Company and dried over sodium sulfate. Solvents were thoroughly purged with dry nitrogen or argon prior to use.

Instrumentation. NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 400.13 MHz or on a Bruker 100 NR operating at 100.13 MHz. ^1H chemical shifts are referred to the residual $CHCl_3$ (7.26 ppm), and ^{13}C chemical shifts are referred to $^{13}CDCl_3$ (77.00 ppm). GC/MS analysis was conducted on a Hewlett-Packard 5970 instrument equipped with mass-selective detector using a 50m (0.18mm I.D.) HP-1 Hewlett-Packard column. Stopped-flow experiments were conducted on a Hi-Tech spectrometer Model SF-3L interfaced to an On-Line Instrument Systems Model 3820 data system. Further details concerning the stopped-flow spectrometer and methodology are given elsewhere.[18] Kinetic experiments were conducted at 25.0 $\pm$ 0.1 ^oC.

Synthesis of cis- and trans-DDA. In a typical experiment, A (170 mg; 0.955 mmole) was dissolved in CCl_4 (40 mL). An NO_2/N_2O_4 solution (2.8 mM NO_2 in equilibrium with 44.6 mM N_2O_4; 18 mL) was slowly added to the solution of A at 25^oC with magnetic stirring under argon or nitrogen atmosphere to rigorously exclude oxygen. A colorless crystalline material that precipitated a few minutes after the addition was completed, consisted almost exclusively of cis-DDA. The trans-isomer is much more

soluble but can be quantitatively crystallized by cooling the reaction mixture down to -20°C overnight. The total yield is typically about 90% with a cis/trans ratio of about 1.0. Cis-DDA can be further purified by recrystallization from $CHCl_3$; trans-DDA can be purified by repeated recrystallization from hexane:CCl_4 (4:1).

Thermolysis of Cis-DDA. A capillary melting point tube (Kimax) was loaded under nitrogen with 5 mg of cis-DDA and the tube mouth was sealed with silicon grease. The tube was then placed in a Mel-Temp melting point apparatus set at 200 °C until a violent evolution of gas ceased and the sample turned from colorless-crystalline to a bright yellow (about 45 seconds). The tube was then allowed to cool down and broken. The contents were dissolved in $CDCl_3$ and analyzed by ^{1}H-NMR and GC/MS.

Crystallographic Measurements and Structure Solution. Crystals of cis-DDA were grown from $CHCl_3$ by slow evaporation. Crystals of trans-DDA were grown by the vapor diffusion method (benzene into $CHCl_3$).

Intensity data were collected by ω - 2θ scans of variable rate designed to yield measurements of equal relative precision for all significant reflections, using an Enraf-Nonius CAD4 diffractometer equipped with CuK_α radiation (λ = 1.54184 Å) and a graphite monochromator. A maximum was placed on the scan time spent on any reflection. One quadrant of data was collected for trans-

DDA and one octant for cis-DDA within the angular limits listed in Table I, which also gives crystal data and specifics for data collection. Data reduction included correction for background reduction, Lorentz, polarization, and absorption, the latter based on psi scans. Data having $I>3\sigma(I)$ were used in the refinements. Structures were solved by direct methods and refined by full-matrix least-squares based on F with weights $w=\sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs. Nonhydrogen atoms were refined anisotropically, while hydrogen atoms were located in difference maps and refined isotropically. The cis-DDA molecule exhibits a rotational disorder of one of the nitro-groups (N1, O1, O2), in which the oxygen atoms are tipped such that they occupy half-populated positions about 0.5 Å out of the mirror plane upon which N1 resides. Attempts to refine an ordered model in noncentrosymmetric space group $Pna2_1$ led to near-unit correlations and lack of convergence. The centrosymmetric group was thus chosen as most appropriate. Final R factors and residuals in final difference maps are given in Table I. Coordinates for the two structures are listed in Table II and III, and the molecules are depicted in Figure 1.

NMR Experiments. The compounds (4 mg) were dissolved in 0.5 mL $CDCl_3$ using 5 mm tubes, and all experiments were done at 25° C. Nuclear Overhauser effect (NOE) and ^{13}C-^{1}H

	cis isomer	trans isomer
Formula:	$C_{14}H_{10}N_2O_4$	$C_{14}H_{10}N_2O_4$
FW:	270.3	270.3
cryst. system:	Orthorhombic	Monoclinic
space group:	Pnma	$P2_1/c$
a, Å:	7.368(1)	7.733(1)
b, Å:	15.163(1)	12.735(2)
c, Å:	10.853(1)	6.383(1)
β, deg:	--	105.58(1)
V, Å^3	1212.5(4)	605.5(2)
Z	4	2
D, g cm^{-3}	1.480	1.482
T, ^oC	25	23
μ, cm^{-1}	8.9	8.9
cryst. size, mm:	0.20x0.36x0.40	0.14x0.19x0.43
min.rel.trans., %:	89.2	94.5
θ limits, deg:	2.75	2.75
scan rates, deg min^{-1}:	180	120
unique data:	1299	1240
observed data:	1101	1082
variables:	129	112
Extinction:	5.5(6)x10^{-6}	8.4(10)x10^{-6}
R:	0.060	0.040
Rw:	0.090	0.055
GOF:	5.62	3.05
max.residual, eÅ^{-3}:	0.41	0.19
Notes:	One NO_2 disordered	--

Table I. Crystal Data and Data Collection Parameters for cis- and trans- 9,10-Dinitro-9,10-dihydroanthracene.

Atom	x	y	z	B(Å^2)
O1	0.3459(4)	0.2772(4)	0.1071(3)	9.0(1)*
O2	0.2164(4)	0.2147(3)	-0.0415(3)	8.2(1)*
O3	-0.0839(3)	0.3202(1)	-0.2296(2)	7.76(5)
N1	0.2170(3)	1/4	0.0608(2)	4.68(5)
N2	-0.1169(4)	1/4	-0.1828(2)	4.52(5)
C1	0.0374(4)	1/4	0.1346(2)	4.35(6)
C2	-0.0648(2)	0.3328(1)	0.1047(2)	4.01(4)
C3	-0.1920(3)	0.3324(1)	0.0098(2)	3.78(4)
C4	-0.2292(4)	1/4	-0.0605(2)	3.76(5)
C5	-0.0343(3)	0.4103(2)	0.1711(2)	5.42(5)
C6	-0.1289(3)	0.4864(2)	0.1412(2)	6.57(5)
C7	-0.2518(4)	0.4865(2)	0.0485(2)	6.09(5)
C8	-0.2863(3)	0.4101(2)	-0.0175(2)	4.91(4)

* Population = 1/2

Table II. Coordinates for cis-9,10-Dinitro-9,10-dihydroanthracene.

Atom	x	y	z	B(Å^2)
O1	0.4345(1)	-0.1267(1)	0.0211(2)	5.30(3)
O2	0.2636(2)	-0.1559(1)	0.2291(2)	5.29(3)
N	0.3054(1)	-0.1064(1)	0.0885(2)	3.26(3)
C1	0.1865(2)	-0.0133(1)	-0.0173(2)	2.58(3)
C2	0.1457(2)	0.0508(1)	0.1608(2)	2.50(3)
C3	-0.0279(2)	0.0602(1)	0.1828(2)	2.46(2)
C4	-0.0576(2)	0.1161(1)	0.3577(2)	3.00(3)
C5	0.0838(2)	0.1635(1)	0.5078(2)	3.44(3)
C6	0.2566(2)	0.1556(1)	0.4841(2)	3.58(3)
C7	0.2878(2)	0.0994(1)	0.3133(2)	3.21(3)

Table III. Coordinates for trans-9,10-Dinitro-9,10-dihydroanthracene

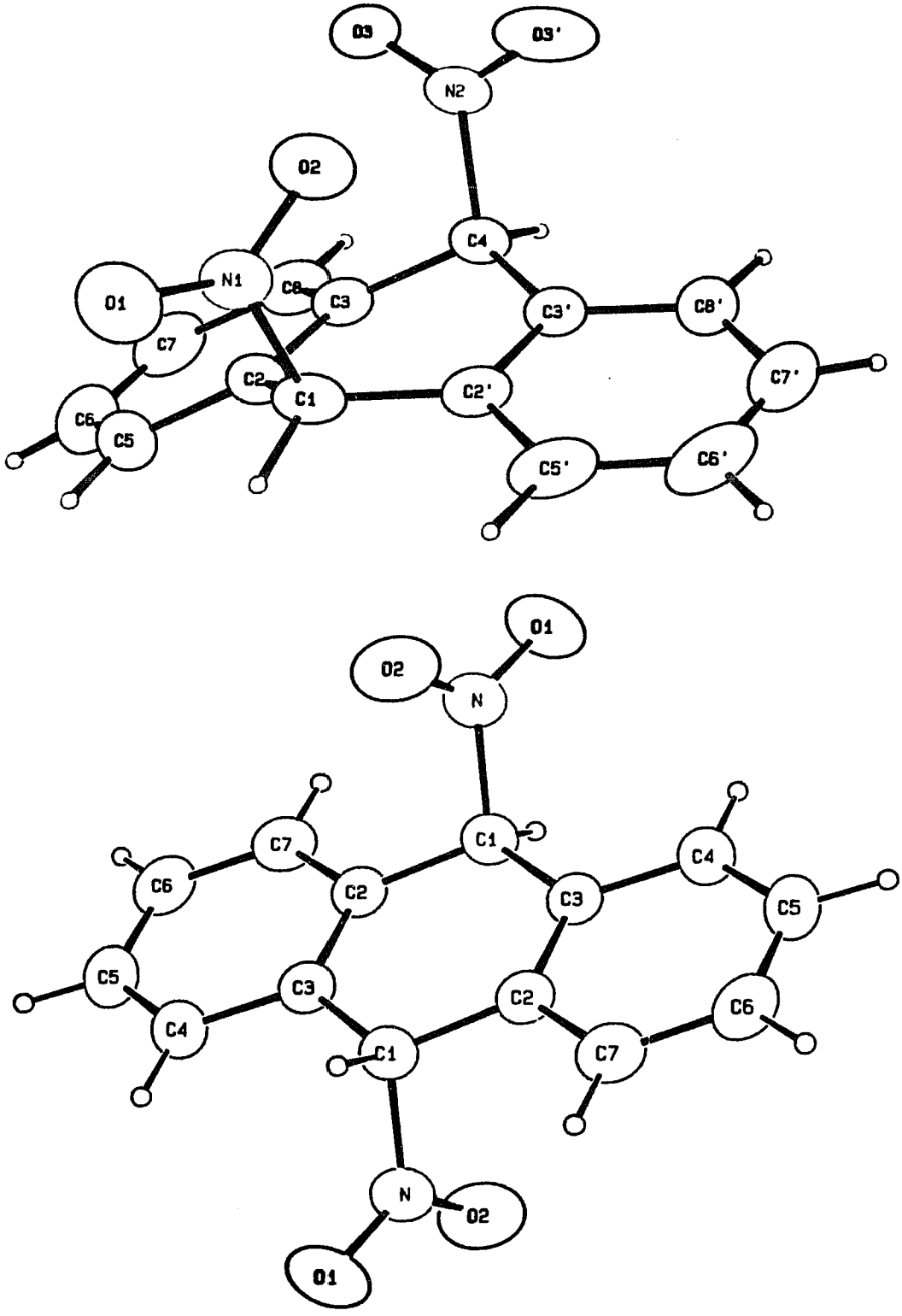


Figure 1. ORTEP drawings of cis- and trans-9,10-dinitro-9,10-dihydroanthracene.

correlation experiments were conducted using Bruker standard software. The NOE were calculated by subtracting the corresponding on and off resonance FID's, Fourier-transforming the difference (with small line-broadening; 0.2 Hz) and relating the enhancement to the area of the same resonance in the control experiment. The ^{13}C-^{1}H correlations were recorded by using a 64 x 4096 data matrix size, 64 increments, and, 128 transients for each t_1 value. Sine bell multiplication was performed in both dimensions prior to Fourier transformation and, an absolute value calculation was done in the F1 dimension of the processed matrix. The recycle time was 2 s. Higher resolution ^{1}H and ^{13}C spectra have been used as projections.

RESULTS AND DISCUSSION

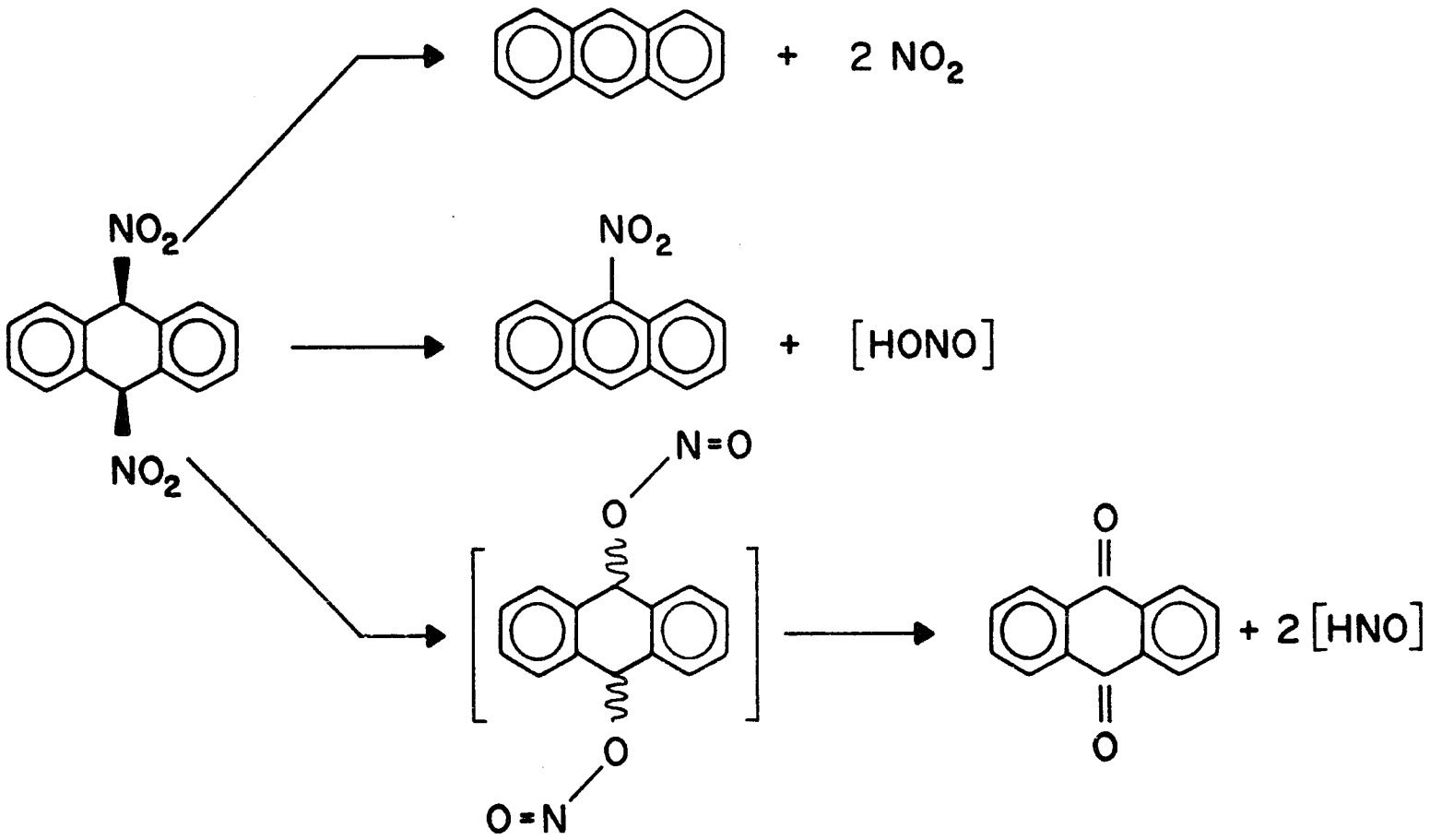
Chemical and Thermal Lability of Cis- and Trans-DDA.

Chromatographic analysis of a mixture of cis- and trans-DDA on silica-gel yields 9NA, a product resulting from their decomposition on contact with the silica-gel. Analysis by GC/FID or GC/MS yields 9NA and anthraquinone (AQ) together with a small amount of A. The relative distributions depend on the injector temperature and the amount of sample injected. Finally, the 200 ^{o}C thermolysis of cis-DDA affords the same products detected by GC-methods. Thus, cis- and trans-DDA are chemically

and thermally labile, and techniques like GC, MS, HPLC, or combination of them, commonly used for the analysis of mixtures of nitrated compounds[12,13,19] cannot be employed. Scheme I describes the thermolytic routes leading to A, 9NA and AQ.

Structural Features of Cis- and Trans-DDA. Nuclear Overhauser effects resulting upon irradiation of H-9,10 or the peri-protons are shown in Table IV. The observed ^1H-^1H NOE also provide the assignments of the ^1H spectrum. The effect observed on the cis-isomer is the larger one, indicating an average shallow boat with pseudoaxial conformational preference for the nitro-groups in solution. The ^1H-^1H NOE's observed for trans-DDA are substantially greater than one-half of the corresponding NOE of the cis-isomer. The trans-DDA NOE's are predicted to be 64% of those of the cis-isomer by using the internuclear distances obtained from the crystallographic study and applying the inverse sixth power relationship of the distance between the irradiated and the observed nuclei. It appears from a comparison of the expected NOE based on the distances in the crystal with the experimental NOE values that the trans-isomer is forced towards an average near-planar conformation in solution. Thus, the single-crystal X-ray diffraction analyses of the isomers of DDA (vide infra) afford results consistent with the expected average solution conformational preferences

SCHEME I



	NOE Results			Chemical Shifts in ppm						
Isomer	Irrad	Obsd	Enh(%)	H-1	H-2	H-9	C-1	C-2	C-9	C-11
cis[b]	H-9	H-1	8	7.75	7.60	6.59	131.17	130.75	86.70	130.16
cis	H-1	H-9	18							
trans	H-9	H-1	6	7.63	7.56	7.03	128.14	130.81	87.73	129.23
trans	H-1	H-9	10							

a) Cis- and trans-9,10-Dinitro-9,10-dihydroanthracene display an AA'BB'system and a singlet.
b) A small positive NOE (1%) was noticed on H-2.

Table IV. NMR Spectral Data for cis- and trans-9,10-Dinitro-9,10-dihydroanthracene.[a]

that were inferred by NMR. The average solution conformations also agree existing force-field calculations[20] and crystal structures of sterically-demanding 9,10-disubstituted-9,10-dihydroanthracenes.[21-23] Trans-9,10-dipropyl-9,10-dihydroanthracene[21] and trans-bis(trimethylsilyl)-9,10-dihydroanthracene[22] were also found to be near planar by X-ray analysis. Similarly, it was found that cis-substituents tend to increase the angle between the planes of the aromatic rings in the butterfly-shaped dihydroanthracene series,[23] inducing planarity as well.

Both isomers of DDA lie on symmetry elements in the solid state, and both exhibit significant flattening of the central ring. The cis-isomer has C_s symmetry in the crystal; thus C2, C3, and their mirror equivalents lie in a common plane with NO_2-substituted carbon atoms C1 and C4 lying 0.338(3) Å and 0.311(2) Å, respectively, out of this plane in a boat deformation. The trans-isomer has crystallographic C_i symmetry, thus the deformation of the central ring is slightly chair-like. Nitro-substituted atom C1 and its inversion equivalent lie $\pm$ 0.055(1) Å from the plane defined by C2, C3, and their inversion equivalents. Maximum deviation from planarity of the aromatic ring is 0.005(2) Å for the cis isomer and 0.007(2) Å for the trans-isomer. The two aromatic rings of the cis-isomer form a dihedral angle of 150.6(1)°,

while those of the trans-isomer are constrained by symmetry to be parallel. The nitro-groups of the trans-isomer form dihedral angles of 97.9(1)^{o} with the best plane of the central ring, and the O1-N-C1-C3 torsion angle is 98.8(2)^{o}. In the case of the cis-isomer, one nitro-group (N2, O3, O3') lies orthogonal to the crystallographic mirror, while the other (N1, O1, O2) is tipped slightly out of the mirror, forming a dihedral angle of 26.9(2)^{o} with it, and resulting in the disorder.

The ^{13}C chemical shifts and assignments are listed in Table IV. The assignments were done using ^{13}C-^{1}H 2D correlations, as shown in Fig 2 and Fig 3. The correlations were optimized for typical values of $^{1}J_{CH}$, and thus, the quaternary carbons shown in the ^{13}C projections do not display a cross peak.

Implications for Nitration Mechanism. Previous studies on the nitration of fluoranthene and naphthalene revealed that the mechanism can be dramatically solvent and temperature dependent.[15-17] The mechanism in CCl_4, at 25 ^{o}C and in the absence of acid catalysis, is best formulated as a homolytic process.[15-17]

The nitration of A with NO_2 in several solvents has often been found to afford substantial amounts of AQ,[2,5,12-14] while other PAH yield none or only traces of quinonoid products.[12-15] Eberson and Radner noticed that the nitration of A with NO_2 in CH_2Cl_2 afforded a much

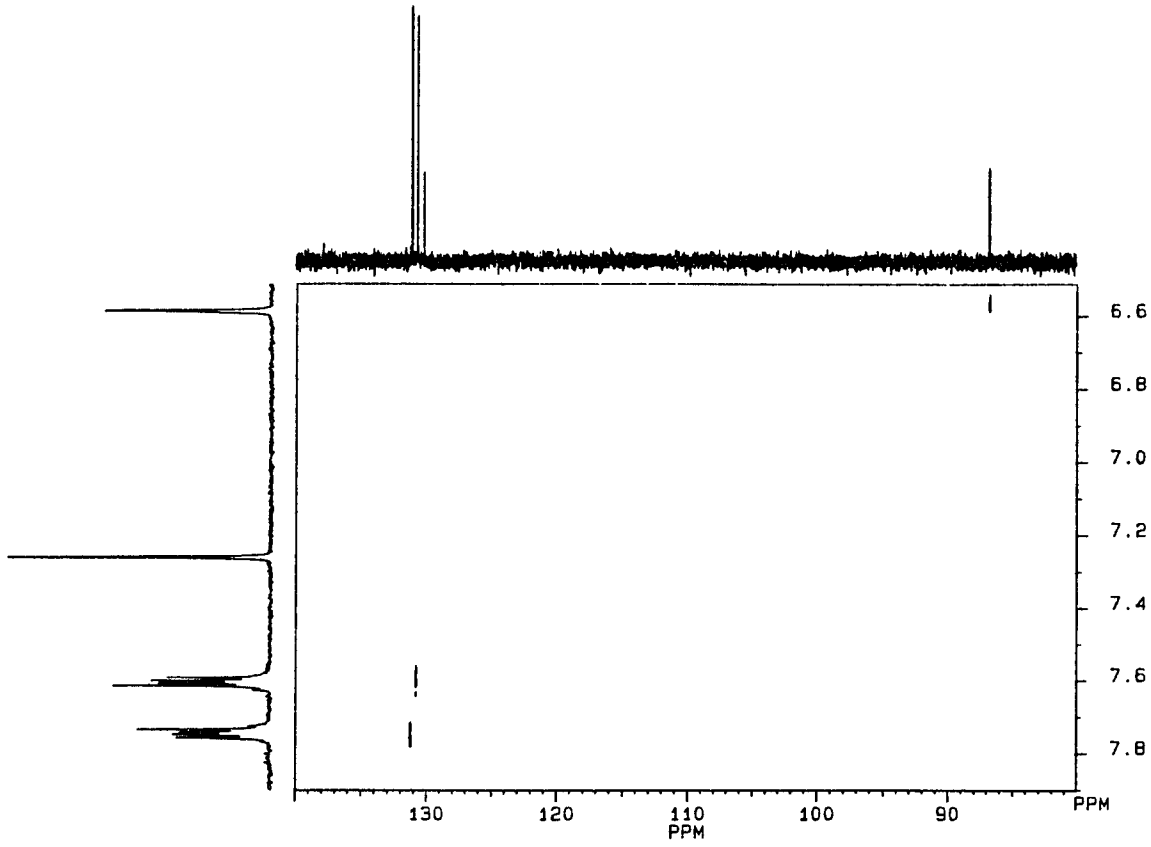


Figure 2. ^{13}C-^{1}H Correlation of cis-9,10-Dinitro-9,10-dihydroanthracene.

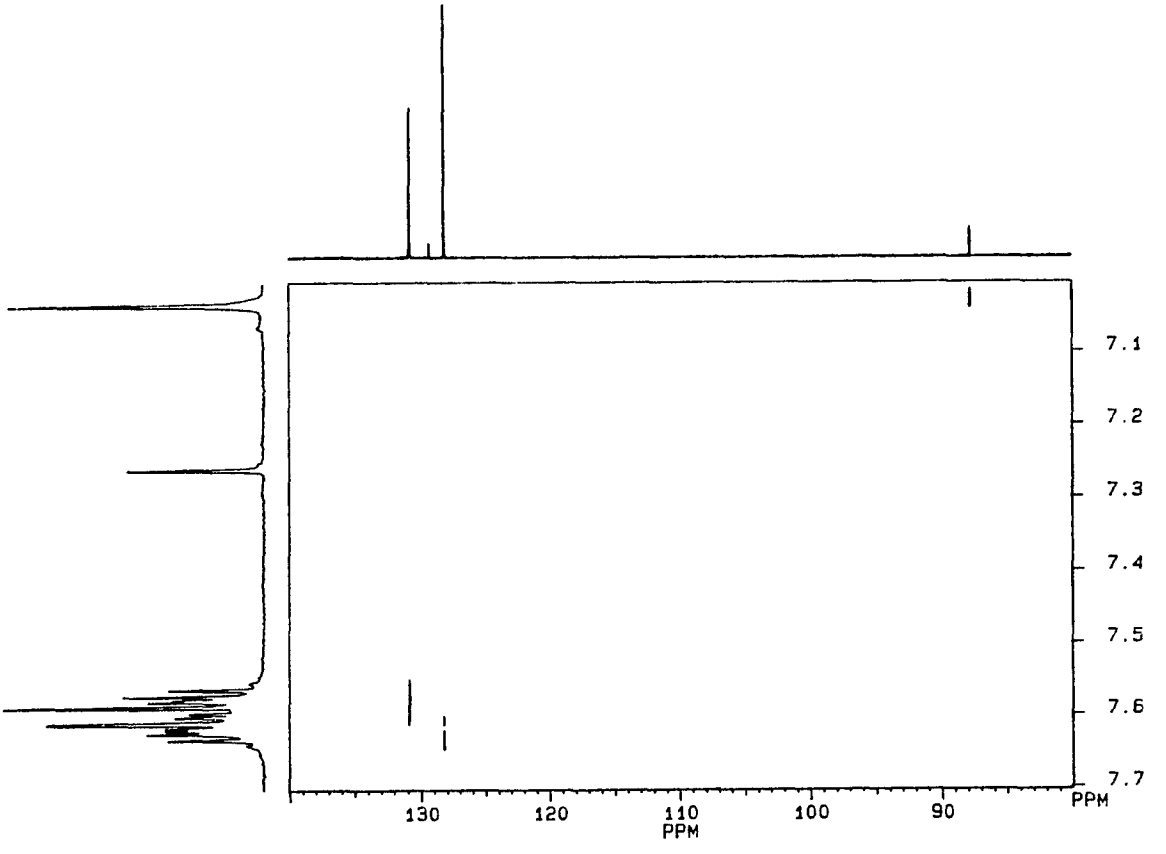


Figure 3. ^{13}C-^{1}H Correlation of trans-9,10-Dinitro-9,10-dihydroanthracene.

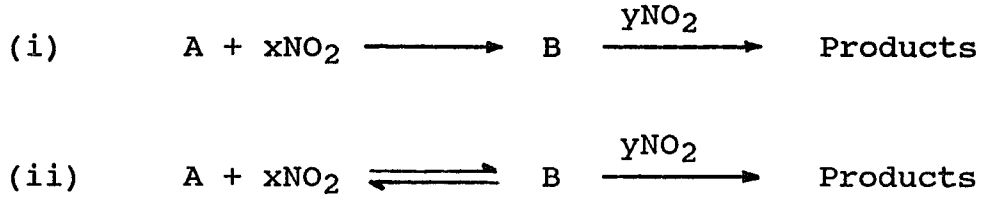
lower yield of mononitroproduct when compared to nitration of other PAH under the same conditions.[12,13] We earlier accounted for the formation of AQ by trapping the incipient radical-cation of A with water and further oxidation under the reaction conditions[14] because the ratio AQ/9NA increased when the reaction was carried out in water-saturated CH_2Cl_2.[24] More recently, Kochi and Masnovi utilized the same argument to explain the formation of related compounds.[25]

Our present studies unambiguously reveal that cis- and trans-DDA are the primary products in CH_2Cl_2, $CHCl_3$ and CCl_4. Under conditions of incomplete conversion, cis- and trans-DDA typically account for about 90% of the material balance of fresh reaction mixtures, with no detectable amounts of AQ or 9NA by ^{1}H-NMR.

The low yield of 9NA observed by Eberson[12,13] is probably due to the combined effects of a non-quantitative thermolysis of DDA to form 9NA, to a reaction stoichiometry different than the one they expected (A:NO_2 ratio of 1:2 instead of their expected 1:1.5), and, at least in part, to trapping of an incipient anthracene radical-cation by adventitious water[14,24,25] (vide infra). Previous reports of various yields of AQ can be explained in a similar manner.

Stopped-flow spectroscopy of the reaction of A with NO_2 in CH_2Cl_2 shows the formation of a transient

intermediate. This intermediate is likely to preceed the formation of the 9-nitro-9-hydroanthryl radical because the coupling of even bulkier hydroanthryl radicals with NO_2 approaches diffusion control.[25] Under pseudo first order conditions in NO_2, at 278 nm,[27] the raw data of Absorbance (D) versus time can be analyzed as two exponentials (formation and decay) in the following manner. Figure 4 shows a typical run from which a single exponential was generated from the end of the apparent decay phase;[28] this exponential, when substracted from the raw data, generates a second exponential (apparent formation). Two kinetic models fit these observations: (i) two pseudo first order series reactions, and, (ii) a first reversible step and neither the fast equilibrium nor the steady state approximations hold.



The equations corresponding to the second case are "unwieldy and of little use for obtaining rate constants from experimental data."[29] Fortunately, a double logarithmic plot of k_{obs} vs NO_2 (in rapid equilibrium with N_2O_4[18]) gives reasonably straight lines for both reaction phases, as can be seen in Figure 5, and as expected for

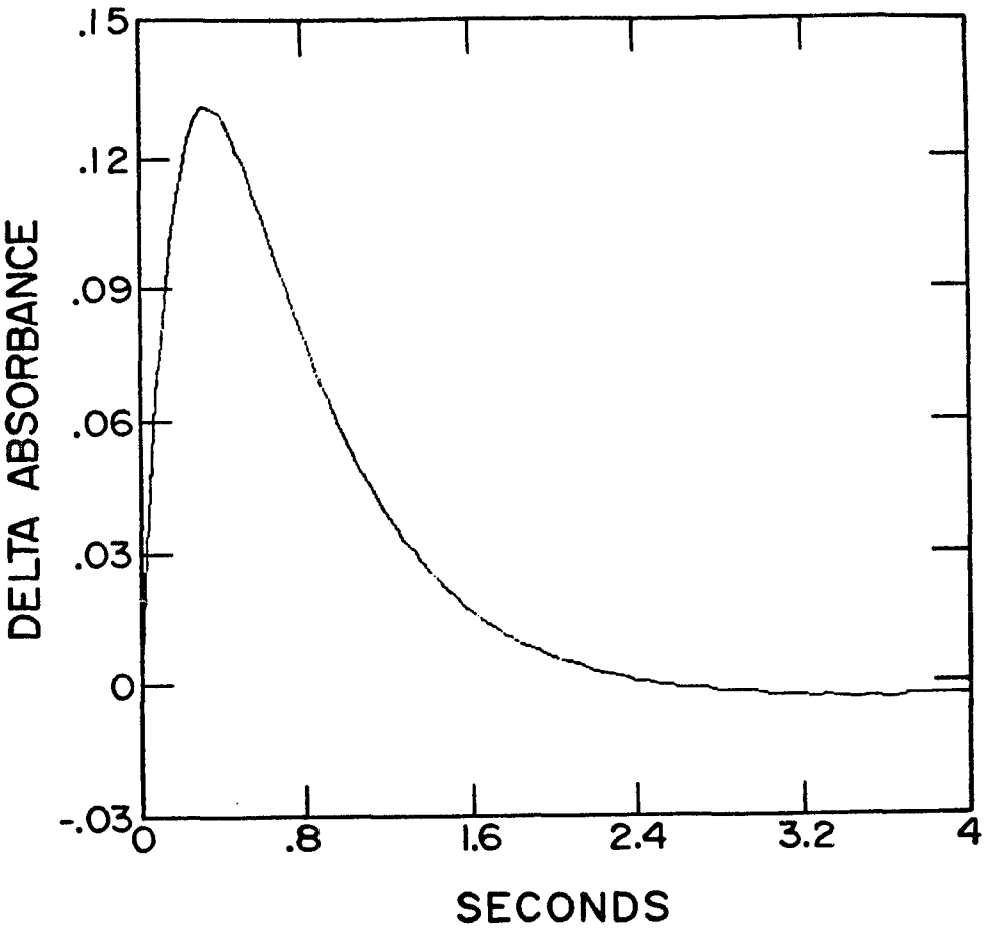
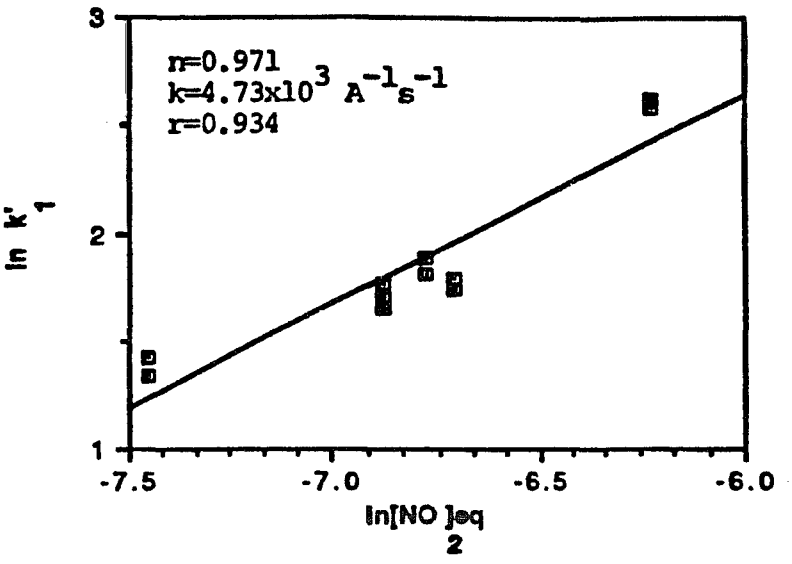


Figure 4. Typical "Rise and Fall" Trace Obtained for the Reaction of Anthracene with NO_2 in CH_2Cl_2 at 25°C.

(a)



(b)

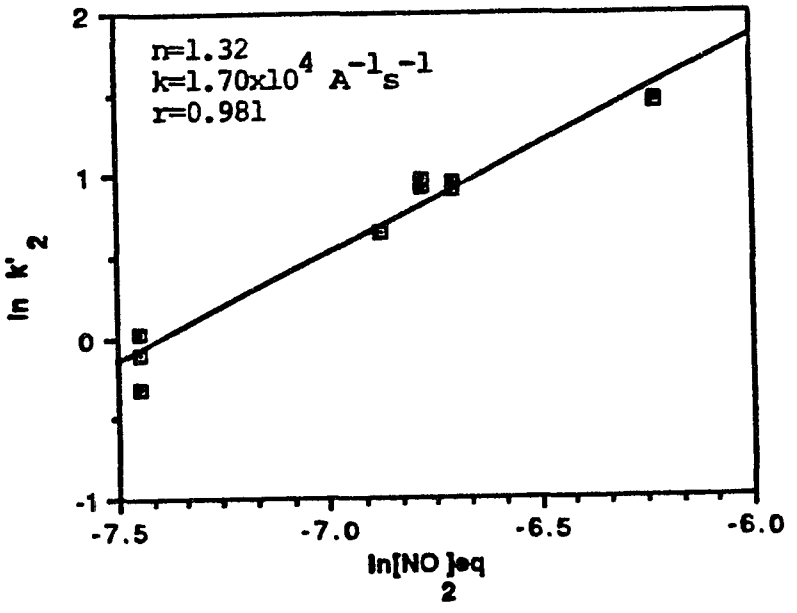


Figure 5. Double natural logarithmic plot of the pseudo first order rates and the concentrations of NO_2 (in equilibrium with N_2O_4) for (a) the apparent early phase and (b) the apparent late phase.

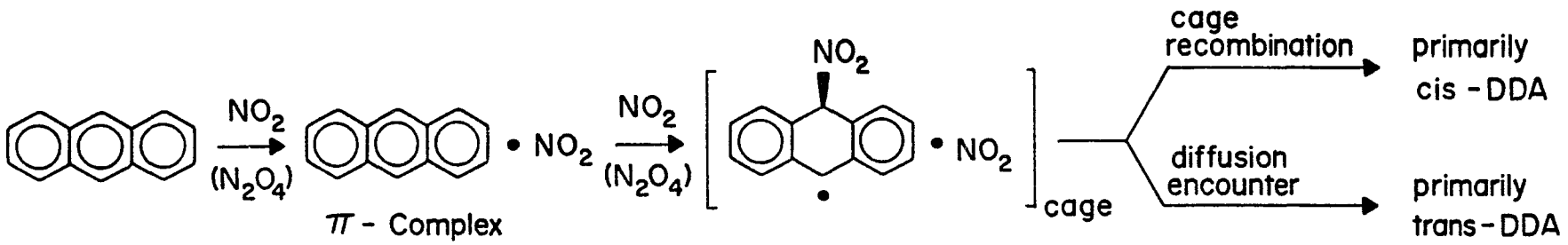
model (i). The order in NO_2 of the apparent first phase is 0.971 (r=0.932; [A]=0.04-0.50 mM) and that of the apparent second phase is 1.32 (r=0.981; [A]=0.04-0.50 mM) and suggest the possibility of some contribution of the undissociated form of NO_2 (N_2O_4), to the apparent later reaction phase. The rate expression is shown in equation (1), where ϵ_A, ϵ_B are the molar absorption coefficients of A and the transient intermediate, and k_1', k_2' are the observed rate constants of the apparent formation and decay phases, respectively.

$$D = U\exp(-k_1't)+V\exp(-k_2't) \qquad (1)$$

where $U = A_o(\epsilon_A-k_1'\epsilon_B/k_1'-k_2')$ and $V = A_ok_1'\epsilon_B/k_1'-k_2'$

A mechanism for this reaction is depicted in Scheme II. The lack of stereoselectivity of the reaction is consistent with the stepwise addition of two molecules of NO_2. The cis-isomer is likely to be formed primarily from cage recombination, whereas the less stable trans-isomer can be rationalized as arising primarily from kinetically-controlled coupling of the free radicals,[30] as is shown in Scheme II. The high regioselectivity of the addition of NO_2 to the middle ring of A is noticeable. Nitrogen dioxide is known to react with organic radicals to form nitro and nitrite products in the gas phase,[31] in the gas-liquid interface[32] and in solution,[33] but coupling at the

SCHEME II


NO2
(N2O4)
π - Complex
• NO2
NO2
(N2O4)
NO2
• NO2
cage
cage recombination
primarily
cis - DDA
diffusion
encounter
primarily
trans - DDA

nitrogen-atom of NO_2 has been regarded as a thermodynamically controlled process in the reaction of NO_2 with aliphatic radicals in the gas phase.[31] Radical coupling at the nitrogen-atom occurs almost exclusively even at near diffusion-control encounters in CCl_4, CH_2Cl_2 and $CHCl_3$.

The isomers of DDA demonstrate the feasibility of the more unstable multiple-addition intermediates previously proposed for the reactions of fluoranthene and naphthalene with NO_2 on the basis of an anomalous product distribution.[15-17] Multiple-addition intermediates reveal a common pattern of the reaction of PAH with NO_2 under neutral conditions and provide further insights into the mechanism of this complex reaction system.

Special care has to be given to drying the solvents and the NO_2 in order to observe the radical reaction pathway because small amounts of Bronsted (NO^+) and Lewis (CH_3SO_3H) acids catalyse an electrophilic pathway[12,34-36] which leads to 9NA and does not require the formation of the isomers of DDA.[37]

Comparison of The Ionic and Radical Nitrations of Anthracene. The nitration of A mediated by the nitronium-ion (or a carrier of it thereof) has been found not to follow the usual pattern observed with other aromatic compunds.[38,39] In fact, the ionic nitration[39] and its radical counterpart, as shown in this work, display "rise

and fall" exponential kinetic profiles. Furthermore, when A was nitrated with nitronium tetrafluoroborate in sulfolane and acetonitrile, the conversion of an intermediate (interpreted by the authors as the 9-nitro-9-hydroanthronium ion) to 9NA was inhibited by the addition of water or diethylether.[38] Later on, Schofield and his coworkers[39] pointed out that an addition-elimination mechanism also fits these observations and the fact that the nitration of A is subject to strong kinetic isotope effect.[38] Thus, it is possible that both the radical and the ionic (provided a suitable nucleophile) nitrations of A occur by addition across the 9- and 10-positions. The adducts of A under ionic nitration conditions are not isolable because the acidic medium facilitates elimination.

Toxicological Implications. Cis- and trans-DDA are expected to be formed as the result of the gas phase reaction of A with NO_2 in polluted tropospheric air. The presence of cis- and trans-DDA in polluted air samples has not been yet assessed due to their thermal lability and their lability to bases and nucleophiles. However, 9NA and AQ, the expected decomposition products, are important atmospheric pollutants.[40]

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We also wish to thank Drs. John Cosgrove and David Giamalva for helpful suggestions.

Supplementary Material Available: Tables of bond distances, bond angles, coordinates for hydrogen atoms, anisotropic thermal parameters, and structure factor amplitudes (27 pages) for cis- and trans-DDA. Ordering information is given on any current masthead page.

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24) Although NO_2 (or N_2O_4) dismutates in water to HONO and HNO_3, if this reaction is slow compared to the trapping of the incipient anthracene radical-cation, the latter might become the only important process. See, for example, Prutz, W. A.; Monig, H.; Butler, J.; Land, E. J. Arch. Biochem. and Bioph. 1985, 243, 125-134.

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27) At 278nm, only A,[26] the first intermediate, and, the 9-nitro-9-hydroanthryl radical[26] are the absorbing species. However, because of its high reactivity, the 9-nitro-9-hydroanthryl radical contribution to the total optical absorbance is expected to be negligible at all times.

28) Whether the reaction consists of a "true" fast formation followed by a slow decay, or vice versa, depends on the magnitude of the absorption coefficient of the intermediate. In fact, the rates of the two kinetic phases of the reaction can be interchanged, providing a second mathematical solution to the problem. Thus, we are

at this point unable to tell which phase has some contribution from the undissociated form of NO_2 (N_2O_4). For further details see Alcock, N. W.;Benton, D. J.; Moore, P. Trans. Faraday Soc. 1970, 66, 2210-2213.

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30) The cis-isomer is the more stable product in which steric interactions of the nitro-groups with the peri-hydrogens are minimized. Attack from the less hindered side yielding trans-DDA can be rationalized as kinetically-controlled diffusive encounters of the 9-nitro-9-hydroanthryl radical and NO_2.

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Chapter III. Supplementary Material.

Atom	x	y	z	B(A^2)
H1	0.092(4)	1/4	0.216(3)	2.8(7)
H4	-0.353(5)	1/4	-0.096(3)	3.8(8)
H5	0.050(3)	0.407(2)	0.237(3)	4.0(6)
H6	-0.121(4)	0.533(1)	0.183(2)	4.5(6)
H7	-0.308(3)	0.534(1)	0.021(2)	4.0(6)
H8	-0.377(3)	0.415(1)	-0.083(2)	2.9(5)

Table I. Coordinates for Hydrogen Atoms in Cis-9,10-dinitro-9,10-dihydroanthracene.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
N1	O1	1.150(2)	C2	C5	1.397(2)
N1	O2	1.233(2)	C3	C4	1.490(9)
N1	C1	1.547(2)	C3	C8	1.399(2)
N2	O3	1.204(1)	C5	C6	1.386(2)
N2	C4	1.564(2)	C6	C7	1.354(2)
C1	C2	1.499(1)	C7	C8	1.386(2)
C2	C3	1.392(1)			

Table II. Bond Distances in Cis-9,10-dinitro-9,10-dihydroanthracene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	N1	O2	123.5(2)	C2	C3	C4	120.41(8)
O1	N1	C1	118.7(1)	C2	C3	C8	119.19(9)
O2	N1	C1	117.6(1)	C4	C3	C8	120.39(9)
O3	N2	O3'	124.3(1)	N2	C4	C3	109.73(6)
O3	N2	C4	117.69(6)	C3	C4	C3'	114.0(1)
N1	C1	C2	108.53(7)	C2	C5	C6	120.0(1)
C2	C1	C2'	113.7(1)	C5	C6	C7	120.7(1)
C1	C2	C3	119.66(8)	C6	C7	C8	120.4(1)
C1	C2	C5	120.81(9)	C3	C8	C7	120.2(1)
C3	C2	C5	119.5(1)				

Table III. Bond Angles for Cis-9,10-dinitro-9,10-dihydroanthracene.

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.052(1)	0.201(6)	0.086(2)	-0.039(2)	-0.007(2)	-0.027(3)
O2	0.071(2)	0.161(4)	0.079(2)	-0.036(2)	0.031(1)	-0.042(2)
O3	0.141(2)	0.098(1)	0.0562(9)	-0.047(1)	0.0309(9)	-0.0077(9)
N1	0.042(1)	0.086(2)	0.051(1)	0	-0.003(1)	0
N2	0.061(1)	0.077(1)	0.033(1)	0	-0.001(1)	0
C1	0.041(1)	0.091(2)	0.034(1)	0	-0.002(1)	0
C2	0.0429(9)	0.069(1)	0.0408(8)	-0.0065(9)	0.0064(7)	-0.0077(9)
C3	0.0442(9)	0.058(1)	0.0413(8)	-0.0008(8)	0.0066(7)	0.0015(8)
C4	0.039(1)	0.069(2)	0.034(1)	0	-0.003(1)	0
C5	0.060(1)	0.087(1)	0.058(1)	-0.021(1)	0.013(1)	-0.023(1)
C6	0.082(1)	0.071(1)	0.096(1)	-0.022(1)	0.044(1)	-0.031(1)
C7	0.079(1)	0.063(1)	0.090(1)	0.002(1)	0.037(1)	0.002(1)
C8	0.060(1)	0.064(1)	0.062(1)	0.008(1)	0.015(1)	0.008(1)

Table IV. Anisotropic Thermal Parameters for Cis-9,10-dinitro-9,10-dihydroanthracene.

Atom	x	y	z	B(A^2)
H1	0.270(2)	0.025(1)	-0.087(2)	0.8(3)
H4	-0.181(2)	0.119(1)	0.374(2)	1.5(3)
H5	0.065(2)	0.201(2)	0.633(2)	2.0(4)
H6	0.350(2)	0.190(2)	0.582(3)	2.3(4)
H7	0.408(2)	0.094(2)	0.296(2)	1.6(3)

Table V. Coordinates for Trans-9,10-dinitro-9,10-dihydroanthracene.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N	1.216(1)	C2	C7	1.402(1)
O2	N	1.211(1)	C3	C4	1.394(1)
N	C1	1.541(1)	C4	C5	1.384(1)
C1	C2	1.500(1)	C5	C6	1.388(1)
C1	C3	1.511(1)	C6	C7	1.378(1)
C2	C3	1.392(1)			

Table VI. Bond Distances for Trans-9,10-dinitro-9,10-dihydroanthracene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	N	O2	124.23(9)	C3	C2	C7	119.27(8)
O1	N	C1	117.27(8)	C1	C3	C2	121.26(7)
O2	N	C1	118.48(7)	C1	C3	C4	118.99(7)
N	C1	C2	107.97(6)	C2	C3	C4	119.74(7)
N	C1	C3	106.20(7)	C3	C4	C5	120.51(8)
C2	C1	C3	116.68(6)	C4	C5	C6	119.80(8)
C1	C2	C3	121.90(7)	C5	C6	C7	120.17(8)
C1	C2	C7	118.80(7)	C2	C7	C6	120.49(8)

Table VII. Bond Angles for Trans-9,10-dinitro-9,10-dihydroanthracene.

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0418(5)	0.084(1)	0.0771(7)	0.0213(6)	0.0182(5)	-0.0091(7)
O2	0.0705(7)	0.0560(8)	0.0759(7)	0.0154(6)	0.0224(5)	0.0271(6)
N	0.0302(5)	0.0444(8)	0.0448(6)	0.0036(5)	0.0027(4)	-0.0070(6)
C1	0.0278(5)	0.0340(8)	0.0363(5)	-0.0005(5)	0.0086(4)	0.0002(6)
C2	0.0309(5)	0.0305(7)	0.0316(5)	-0.0004(5)	0.0046(4)	0.0008(6)
C3	0.0317(5)	0.0301(7)	0.0302(5)	0.0005(5)	0.0061(4)	0.0020(5)
C4	0.0419(6)	0.0371(8)	0.0350(6)	0.0026(6)	0.0104(5)	-0.0007(6)
C5	0.0571(7)	0.0380(9)	0.0330(6)	0.0038(7)	0.0077(5)	-0.0043(6)
C6	0.0477(7)	0.0417(9)	0.0371(7)	-0.0022(7)	-0.0051(6)	-0.0052(7)
C7	0.0333(6)	0.0409(8)	0.0428(6)	-0.0017(6)	0.0021(5)	-0.0017(7)

Table VIII. Anisotropic Thermal Parameters for Trans-9,10-dinitro-9,10-dihydroanthracene.

CHAPTER IV. FREE RADICAL NITRATION OF NAPHTHALENE WITH NITROGEN DIOXIDE IN CCl_4

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August 31, 1988

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Please find three copies of a manuscript we would like you to consider as an article for JOC. In this manuscript, we report on the free radical nitration of naphthalene with NO_2 in carbon tetrachloride. This novel nitration system is characterized by low 1-nitronaphthalene/2-nitronaphthalene ratios and the unexpected formation of 1,3- and 2,3-dinitronaphthalene, even at low conversions. The nitration of polycyclic aromatic hydrocarbons (PAH) with NO_2 in carbon tetrachloride produces nitro-PAH that are identical to some that have been identified in environmental samples but cannot be explained by the conventional electrophilic mechanism of nitration. We propose these products are formed by free radical nitrations.

I suggest these persons as knowledgeable referees:

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Enclosure: Three copies of MS #8819

ABSTRACT

The nitration of naphthalene (NAP) with nitrogen dioxide in carbon tetrachloride occurs via a free radical mechanism, involving metastable adducts of NAP and two to four moles of NO_2 per mole of NAP. This free radical nitration system is characterized by: (1) low 1-nitronaphthalene/2-nitronaphthalene (1NNAP/2NNAP) ratios and (2) the formation of unexpected dinitronaphthalene isomers, 1,3-dinitronaphthalene (1,3-diNNAP) and 2,3-dinitronaphthalene (2,3-diNNAP), at low conversions. There is strong steric repulsion of the nitro groups in the ORTEP drawing of the 2,3-diNNAP crystal structure (Fig 1). The elimination of HNO_2 from a postulated tetranitrotetrahydronaphthalene intermediate is, therefore, suggested to occur under kinetic control. The nitro substitutent has a small activating effect towards free radical nitration in 2NNAP while it has no noticeable effect in 1NNAP, contrasting sharply with conventional electrophilic nitration where the nitro substituent has a very strong deactivating effect. An ionic electrophilic reaction mechanism predominates in solvents of higher polarity and is subject to efficient acid catalysis. We suggest our conditions of free radical nitration model the gas phase atmospheric free radical nitration of NAP, where low 1NNAP/2NNAP ratios and 1,3-diNNAP also have been

reported.

The nitration of naphthalene (NAP) has been the subject of several studies that have contributed to our current knowledge of the mechanisms of the nitration of aromatic hydrocarbons.[1-14] However, the nitration of NAP by nitrogen dioxide[15] under free radical conditions (e.g., neutral conditions in solvents of low polarity) has not been studied in detail. The literature contains a few reports on the nitration of NAP with nitrogen dioxide under various conditions, including the reaction of solid NAP with liquid N_2O_4[16] and the reaction of NAP with NO_2 in CH_2Cl_2[12,13,17] or in more polar solvents like acetonitrile[1] and sulfolane.[5-7] Barlas and his collaborators investigated the photochemical reactions of NAP with NO_2 in CCl_4,[18] but their studies were complicated by reactions of reactive intermediates with the solvent.

Recently, free radical nitration of polycyclic aromatic hydrocarbons (PAH) has attracted the attention of the environmental community because of the identification of unexpected NO_2-PAH in samples of ambient particulate organic matter (POM)[19,20] that cannot be explained in terms of the classical ionic electrophilic mechanism of nitration. We have reported that the nitration of fluoranthene[21,22] and anthracene[23] by NO_2 in CCl_4 involves radical intermediates and, judged from the products obtained, models the nitrations that occur in the atmosphere. Therefore, we have undertaken a more complete

study of the nitration of NAP with NO_2 in CCl_4.

RESULTS AND DISCUSSION

The 1-Nitronaphthalene/2-Nitronaphthalene (1NNAP/2NNAP) Ratio. The 1-nitronaphthalene/2-nitronaphthalene (1NNAP/2NNAP) ratios obtained under several nitration conditions are illustrated in Table I. The reaction of NAP with liquid N_2O_4 at 18-20 ^oC has been reported to yield 1NNAP exclusively. The nitration of NAP with NO_2 in CCl_4 gives an 1NNAP/2NNAP ratio similar to that obtained in nitrations by the nitronium-ion (or a strongly solvated modification thereof). It also affords a 1NNAP/2NNAP ratio markedly lower than that obtained with NO_2 in more polar solvents like sulfolane or acetonitrile. High 1NNAP/2NNAP ratios have also been reported for the nitration of NAP with NO_2 in CH_2Cl_2.[12,13,17] However, when 2,6-di-tert-butylpyridine (DTBP) is used as scavenger of acids[24] in CH_2Cl_2, a lower 1NNAP/2NNAP ratio (about 4) is obtained, and the reaction rate is also slower, comparable to that obtained in CCl_4. (DTBP does not significantly change the products when the nitration is carried out in CCl_4.) Thus, nitric and/or nitrous acid are efficient catalysts of an ionic nitration pathway in solvents more polar than CCl_4.

The Formation of Unusual Dinitronaphthalenes at Low Conversions. The most striking feature of the nitration

Reagent	Solvent	Temp[a]	1NN/2NN	Ref.
NO_2BF_4	Sulfolane	25	10	1
NO_2BF_4	Nitromethane	25	12	1
$C(NO_2)_4$	Gas phase	300	1	1
NO_2	Acetonitrile	25	24	1
NO_2	Sulfolane	25	19	7
NO_2	CH_2Cl_2	b	24	17
NO_2	CH_2Cl_2[c]	25	4	d
NO_2	CCl_4	25	10	d
NO_2	CCl_4[c]	25	8	d
NO_2	CCl_4	50	4.5	d
NO_2	No solvent	18-20	e	16
HNO_3	H_3PO_4	25	5-6	15
HNO_3	AcOH	50	16	f
HNO_3	Ac_2O	50	8	f

a) ^oC. b) Room temperature c) 2,6-Di-tert-butylpyridine was added to scavenge nitric and nitrous acids. d) This work. e) Exclusive formation of 1-nitronaphthalene was reported. f) Streitweiser, A., Jr.; Fahey, R. C. J. Org. Chem. 1962, 27, 2352-2355.

Table I. Nitration of Naphthalene under Different Conditions.

of NAP with NO_2 in CCl_4 is the formation of the unexpected 1,3-dinitronaphthalene (1,3-diNNAP) and 2,3-dinitronaphthalene (2,3-diNNAP) even at low conversions. The formation of these dinitronaphthalenes in the nitration of NAP is unprecedented.

Under conditions of conventional electrophilic nitration, benzene reacts with HNO_3/H_2SO_4 about 10^9 times faster than does nitrobenzene.[25] Therefore, if dinitration of NAP were to occur by an electrophilic mechabism, the second nitro group would be expected to add to the unsubstituted ring of the nitronaphthalene. Furthermore, the nitro group is meta-director. The formation of 1,3-diNNAP and 2,3-diNNAP thus violates the well established rules of conventional electrophilic nitration.

Mechanistic Considerations. A change in the nitration mechanism with changing solvents is suggested by two observations. Firstly, the 1NNAP/2NNAP ratio becomes lower as the solvent polarity is lowered or upon the addition of the non-nucleophilic base DTBP. Secondly, dinitronaphthalenes are not formed in the acid-catalysed nitration of NAP by NO_2 in CH_2Cl_2.[12,13,17] With NO_2 in CCl_4, dinitronaphthalenes are formed at low conversions. The operation of an ionic electrophilic mechanism in CCl_4 can be ruled out because, under these conditions, the nitro group is a meta-director with strong deactivation.

As can be seen in Table II, the diNNAP's substitution pattern obtained with NO_2 in CCl_4 contrasts sharply with those obtained by nitration of 1NNAP and 2NNAP with HNO_3/H_2SO_4.[26]

Many free radical aromatic substitutions are facilitated by both electron-releasing and -withdrawing substituents. Therefore, the product distributions of the nitration of 1NNAP and 2NNAP also were studied to investigate the possibility of a two-step free radical nitration. At 25 ^oC, the reactivity of 1NNAP towards NO_2 is comparable to that of NAP and about 8-times slower than that of 2NNAP. The nitration of 1NNAP to about 4% conversion yields a complex mixture of seven diNNAP's and four trinitronaphthalenes, but was not investigated further. The nitration of 2NNAP yields 1,3-diNNAP and 2,3-diNNAP. Table II shows the product distribution of the nitration of NAP at 25 ^oC and 50 ^oC and of 2NNAP at 25 ^oC. The product distribution of the nitration of NAP remains unchanged up to about 15% conversion. Thus, the production of diNNAP's occurs too early in the nitration of NAP in CCl_4 for their formation to arise from further free radical nitration of either 1NNAP or 2NNAP.

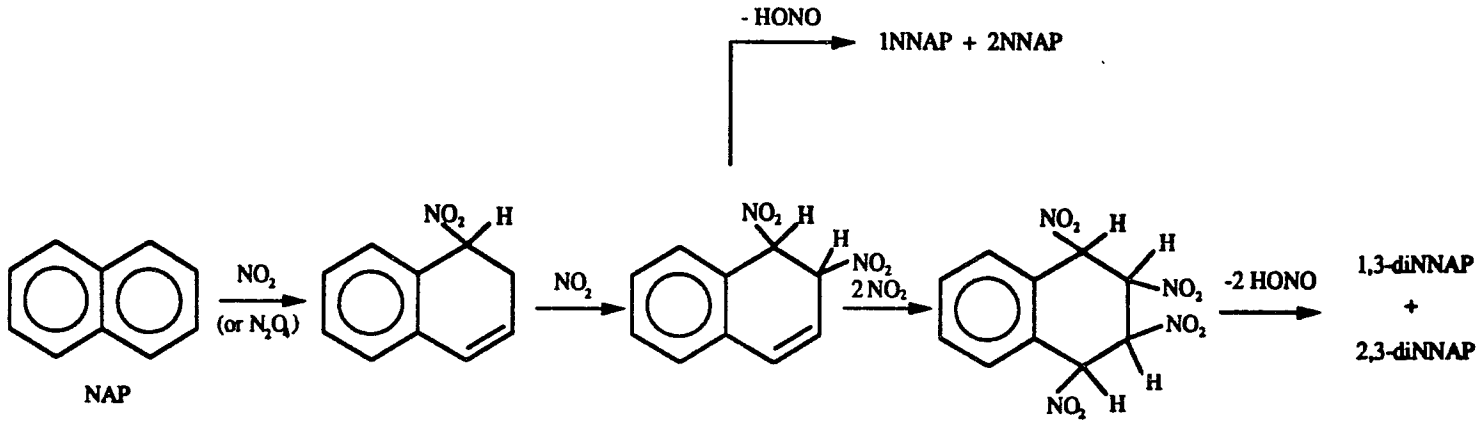
Schemes I and II show multi-step, radical addition-elimination mechanisms that explain the formation of the observed products from the reaction of NAP and 2NNAP with NO_2 in CCl_4, respectively. We proposed a similar

Subs.	Solvent	Reagent	Temp.[a]	Time[b]	Conv.[c]	Yield[c]	NNAP 1	NNAP 2	diNNAP 1,3	diNNAP 2,3	diNNAP 1,5	diNNAP 1,6	diNNAP 1,7	diNNAP 1,8
NAP[d]	CCl_4	NO_2[e]	25	24	12	95[f]	58	6	19	16	-	-	-	-
NAP[g]	CCl_4	NO_2[e]	25	25	12	95[f]	57	6	19	18	-	-	-	-
NAP[h]	CCl_4	NO_2[i]	50	15	7	95[f]	24	9	33	34	-	-	-	-
NAP[j]	CCl_4	NO_2[k]	50	16	6	95[f]	31	7	31	31	-	-	-	-
NAP[h]	CCl_4	NO_2[i]	50	39	9	95[f]	27	6	29	38	-	-	-	-
2NNAP[d]	CCl_4	NO_2[e]	25	21	8	56	-	-	67	33	-	-	-	-
1NNAP[l]	H_3PO_4	HNO_3	0	-	-	-	-	-	-	-	31	-	-	69
2NNAP[l]	H_3PO_4	HNO_3	0	-	-	-	-	-	-	-	-	42	52	-

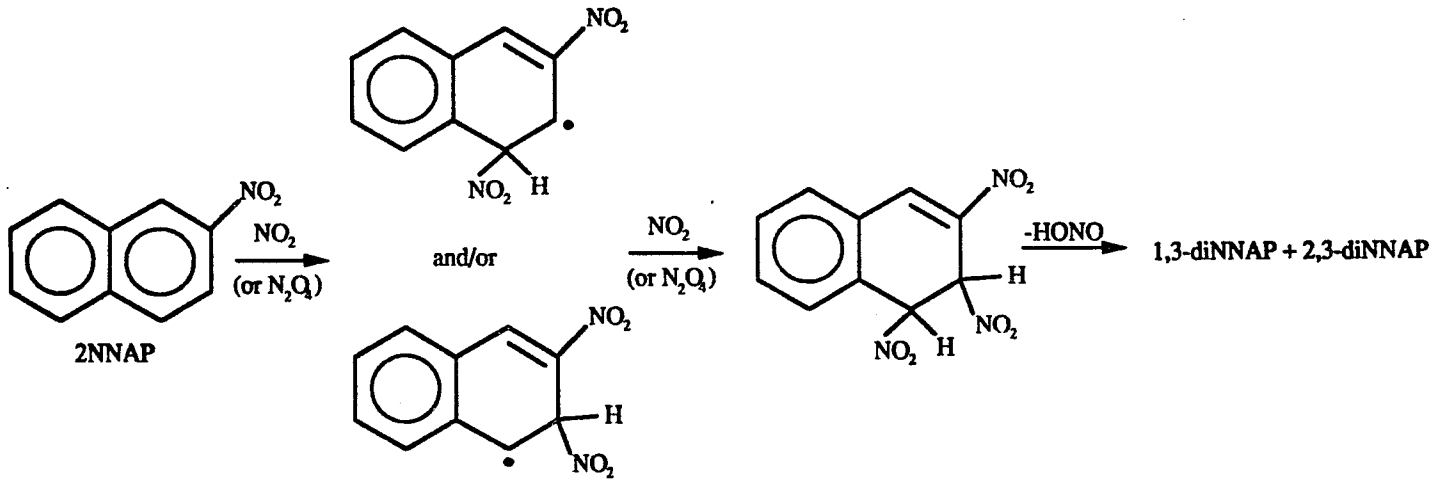
a) ^{o}C b) hrs. c) percentage d) 2.0 M; 1.5 mL e) 2 M; 2.4 mL; concentration of NO_2 denotes total N(IV) in the equilibrium mixture of NO_2 and N_2O_4 f) A small amount of a naphthoquinone and of a third dinitronaphthalene, identified as 1,4-dinitronaphthalene by a best-match algorithm provided with the Hewlett-Packard MS software, account for the remaining 5% g) 2.7 M; 1.5 mL h) 3.4 M; 1.3 mL i) 1 M; 2.5 mL j) 2.1 M; 2.0 mL k) 1 M; 1.5 mL l) Ref. 26.

Table II. Distribution of Nitro- and Dinitronaphthalenes in the Nitration of Naphthalene and Nitronaphthalenes.

Scheme I


- HONO
1NNAP + 2NNAP
NO2
(or N2O4)
NO2
2 NO2
-2 HONO
1,3-diNNAP
+
2,3-diNNAP
NAP

Scheme II


NO2
NO2
(or N2O4)
2NNAP
and/or
NO2
H
NO2
NO2
(or N2O4)
NO2
H
NO2
H
NO2
-HONO
1,3-diNNAP + 2,3-diNNAP

mechanism for the nitration of fluoranthene under comparable conditions.[21,22]

Further addition of NO_2 to the dinitrodihydro intermediate in Scheme I has a stronger temperature dependance than elimination of HNO_2; that is, the addition of NO_2 to the double bond of the newly formed styrene moiety has a larger activation energy than does the elimination of HNO_2 from it. Thus, as can be seen in Table II, the dinitronaphthalenes yields increase as the temperature is raised from 25 ^oC to 50 ^oC.

Although the adducts of two to four NO_2 groups to NAP (and the adducts to the naphthalene moiety of fluoranthene[21,22]) are not isolable, anthracene yields cis- and trans-9,10-dinitro-9,10-dihydroanthracene, due to the smaller aromatization energy of its middle ring.[23] The adducts of NO_2 and anthracene thus provide further indirect proof for our proposed multiple addition intermediates in the radical nitration of naphthalene and fluoranthene. Multiple addition intermediates of varying stability appear to be a common pattern in the radical nitration of PAH, contrasting sharply with electrophilic nitration where σ-complexes normally lose their acidic proton before nucleophilic capture can take place.

The nitrations of NAP and of 2NNAP with NO_2 in CCl_4 are synthetically useful and lead to two diNNAP's in one step. Previous syntheses of 2,3-diNNAP involved

bromination-dehydrobromination of 1,2,3,4,-tetrahydro,2,3-dinitronaphthalene[27] or of 1,2,3,4-tetrahydro,6,7-dinitronaphthalene,[28] both of which are not easily accesible starting materials. Existing methods for the synthesis of 1,3-diNNAP involve one of these multiple step routes: a) the dinitration of 1-naphthol followed by transformation to the chloride and, finally, dehalogenation by Cu-powder in molten organic acid;[29] b) dinitration and cracking of the Diels-Alder adducts of naphthalene and hexachlorocyclopentadiene;[30,31] and, c) peracid oxidation of the corresponding diamine or nitroamine to 1,3-diNNAP.[32]

Kinetically-Contolled Elimination. We have conducted a single crystal X-ray study of 2,3-diNNAP to investigate the steric interactions at the sites of substitution. The ORTEP drawing of the crystal structure of 2,3-diNNAP shows strong steric hindrance (Fig 1). The nitro substituents are rotated significantly out of the best plane of the naphthalene ring system, forming dihedral angles of 33.0(1)^{o} (for N1) and 47.5(1)^{o} (for N2) with that plane. The two nitro groups best planes, calculated including the nitro-substituted carbon atoms, intersect with a dihedral angle of 51.8(2)^{o}. Similar out-of-plane rotations of nitro substituents adjacent to each other on benzene rings occur in hexanitrobenzene,[33] 4-chloro-1,2-dinitrobenzene,[34] and 2,3,4,6-tetranitroaniline.[35] The

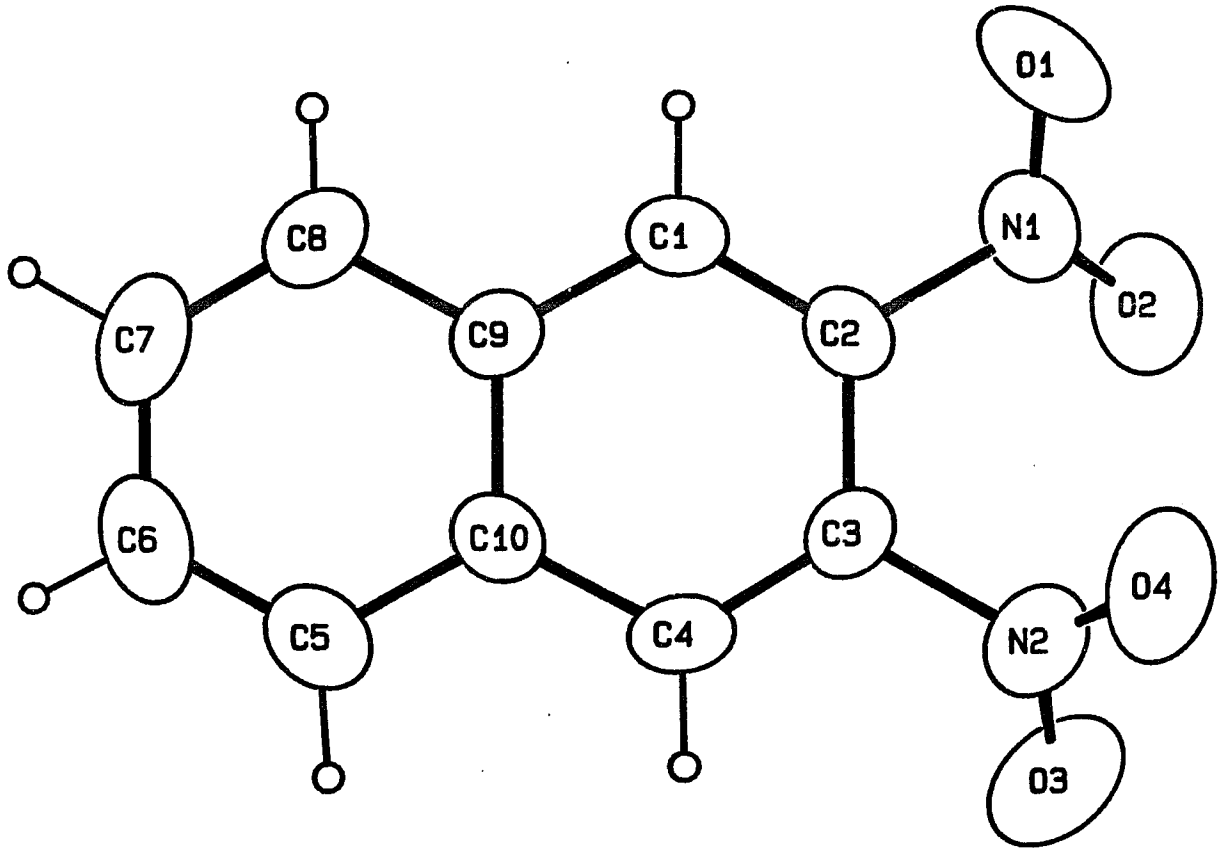


Figure 1. ORTEP drawing of the X-ray structure of 2,3-dinitronaphthalene showing the orientation of the nitro groups.

naphthalene ring is measurably nonplanar, with an average deviation from the best plane 0.009(1)Å, and a maximum deviation 0.021(2)Å for C3, one of the nitro-substituted carbon atoms. The two nitrogen atoms lie on either side of this plane, at distances of 0.150(3)Å for N1 and 0.219(3)Å for N2. Bond distances within the naphthalene nucleus exhibit the pattern of long and short values observed in 1,8-dinitronaphthalene[36] and 1,5-dinitronaphthalene,[37] as well as in naphthalene[38] itself. While the N1-O2 and N2-O4 distances within the nitro groups are normal at 1.230(2) and 1.234(2)Å, respectively, the N1-O1 and N2-O3 are shortened at 1.203(2) and 1.196(2)Å. Since none of the analogous compounds mentioned above exhibit this shortening, and since oxygen atoms O1 and O3 have the largest thermal parameters of the structure (B=9.28 and 9.03Å^2, respectively), we feel that this shortening is an artifact of the thermal motion.

The formation of the very unexpected vicinal-dinitroaromatic hydrocarbons is characteristic of the NO_2/CCl_4 nitration system for both NAP and fluoranthene. (Fluoranthene yields 1,2-dinitrofluoranthene among other products.) We propose that these hindered vicinal dinitro species arise from the kinetically-controlled regiospecific elimination of nitrous acid from the metastable multiple addition intermediates. Elimination of nitrous acid in the tetranitrotetrahydronaphthalene

intermediate is likely to start by the weakening of one of the C-N bonds at the benzylic positions, where a partial positive charge can be stabilized by resonance, as suggested by the presence of only very small amounts of a third dinitronaphthalene, identified as 1,4-diNNAP (Table II).

Environmental Relevance. It has been found that two- to four-ring PAH produced from gasoline-fueled vehicles occur mainly in the gas phase.[39] Nitrogen dioxide is also an important atmospheric pollutant produced by a variety of anthropogenic activities including fossil fuel combustion and biomass burning. We suggest that our reaction conditions model free radical gas phase atmospheric reactions of NAP and NO_2, and probably other PAH as well.[21-23] Mutagenic nitro- and dinitronaphthalenes[40,41] are known to be produced in the atmosphere, and low 1NNAP/2NNAP ratios[19] and 1,3-diNNAP[20] have been reported in urban ambient air, just as we have observed in CCl_4.

EXPERIMENTAL SECTION

Materials and Methods. Carbon tetrachloride (Mallinckrodt Analytical Reagent) was dried over molecular sieves. Methylene chloride (Mallincrodt ChromAr HPLC) was dried over sodium sulfate, distilled, and stored over molecular sieves. Solvents were thoroughly purged with

dry nitrogen prior to use. Naphthalene (Fischer, scintillation grade) and 2,6-diterbutylpyridine (Aldrich) were used without further purification. Dinitrogen tetroxide (MCB) was distilled until a pure white solid was obtained, indicating that it was freed of lower nitrogen oxides. The purified N_2O_4 was stored in bulbs with teflon stopcocks over phosphorus pentoxide (Alfa). The ^{1}H-NMR spectra were recorded in $CDCl_3$ on a 100 MHz NR Bruker spectrometer, using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS. Yields and product distributions were determined by GC on a Varian 3700 gas chromatograph with a 30 m DB-5 J&W capillary column and interfaced to a Varian CDS 111 integrator. Relative response factors to the FID detector were determined using the purified compounds. GC/MS analyses were conducted on a Hewlett-Packard 5970 STET using a 20 m DB-17 J&W capillary column. Separation of dinitronaphthalenes can be easily performed by silica gel column chromatography using hexane-methylene chloride mixtures. 1,3-Dinitronaphthalene elutes prior to 2,3-dinitronaphthalene in all chromatographic methods tried here.

General Nitration Protocol. A solution of NO_2 in CCl_4 (1.5-2.5 mL; 1-2 M) was added under nitrogen to a solution of naphthalene or nitronaphthalene in CCl_4 (1.3-2.0 mL; 2.0-3.4 M) in a septum-capped vial via a syringe.

A similar protocol was used for the run in methylene chloride, where the solution of NO_2 was spiked with ca. 2% 2,6-di-tert-butylpyridine (relative to the moles of naphthalene employed) prior to mixing with the solution containing the naphthalene. A similar protocol was used to determine the relative reactivity of 1- and 2-nitronaphthalene towards nitrogen dioxide, which was calculated by GC without an internal standard, and has therefore to be regarded as semiquantitative.

X-Ray Experimental. Data were collected from a pale yellow crystal 0.15 x 0.18 x 0.72 mm on an Enraf-Nonius CAD4 diffractometer equipped with MoKα radiation (λ=0.71073 Å) and a graphite monochromator. Crystal data are $C_{10}H_6N_2O_4$, FW=218.2, monoclinic space group $P2_1/n$, a=6.879(2), b=14.802(2), c=9.5511(11)Å, β=91.81(2)°, V=972.0(5)Å^3. Z=4, Dc=1.491 g cm^{-3}, μ=1.1 cm^{-1}, T=22°C. Scan rates varied 0.50-4.0 °/min for ω-2θ scans within 1°<θ<30°, in one quadrant. Of 2832 unique data, 1732 had I>σ(I), and were used in the refinement. Data reduction included corrections for background, Lorentz, and polarization effects. The structure was solved by direct methods and refined by full-matrix least squares based on F with weights w=σ^{-2}(Fo), using the Enraf-Nonius SDP. Nonhydrogen atoms were treated anisotropically. Hydrogen atoms were located by ΔF, and were refined isotropically. At convergence, R=0.072 for 169 variables, and the maximum

residual density was 0.34 e A^{-3}. Coordinates are given in Table III, and further data are given in supplementary material.

1,3-dinitronaphthalene: ^{1}H-NMR (100 MHz, $CDCl_3$) δ 9.07 (d, 1 H, J(2,4)=2 Hz, H2); 8.98 (d, 1 H, H4); 8.64 (br d, 1 H, J(7,8)=8Hz, H8); 8.21 (br d, 1 H, J(4,5)=8Hz, H4); 7.98 (m, 1 H, H7); 7.82 (m, 1 H, H5); MS, m/z (relative intensity) 218 (M^+, 80), 201 (73), 172 (26), 171 (30), 142 (14), 127 (16), 126 (100), 125 (33), 114 (44), 113 (20).

2,3-dinitronaphthalene: ^{1}H-NMR (100 MHz, $CDCl_3$) δ 8.46 (br s, 2 H, H1); 7.97-8.18 (m, 2 H, H6); 7.65-7.95 (m, 2 H, H7); MS m/z (relative intensity) 218 (M^+, 100), 188 (14), 160 (4), 144 (19), 130 (27), 127 (7), 126 (63), 115 (9), 114 (88), 113 (22).

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Supplementary Material Available. Tables with full coordinates, bond distances, bond angles, and anisotropic thermal parameters for 2,3-dinitronaphthalene (8 pages).

Atom	x	y	z	B(Å^2)
O1	0.2661(5)	0.4186(2)	0.0672(2)	9.28(8)
O2	0.1006(4)	0.3008(2)	0.1216(2)	6.94(6)
O3	0.1772(5)	0.1654(2)	0.4159(3)	9.03(8)
O4	0.3919(4)	0.2067(2)	0.2722(3)	7.00(6)
N1	0.2022(4)	0.3668(2)	0.1512(2)	5.03(5)
N2	0.2665(4)	0.2231(2)	0.3583(3)	5.27(6)
C1	0.2375(3)	0.4751(2)	0.3407(2)	3.30(5)
C2	0.2342(4)	0.3870(2)	0.2999(2)	3.29(5)
C3	0.2427(3)	0.3173(1)	0.4001(3)	3.26(5)
C4	0.2499(4)	0.3366(2)	0.5383(3)	3.47(5)
C5	0.2631(4)	0.4499(2)	0.7287(3)	4.24(6)
C6	0.2703(4)	0.5377(2)	0.7689(3)	4.88(6)
C7	0.2665(4)	0.6073(2)	0.6698(3)	4.70(6)
C8	0.2558(4)	0.5885(2)	0.5302(3)	3.85(5)
C9	0.2488(3)	0.4978(1)	0.4838(2)	2.95(4)
C10	0.2531(3)	0.4273(2)	0.5852(2)	3.09(4)
H1	0.237(3)	0.521(2)	0.273(3)	4.5(6)
H4	0.253(3)	0.290(2)	0.605(3)	4.7(6)
H5	0.270(4)	0.397(2)	0.796(3)	5.0(6)
H6	0.277(4)	0.554(2)	0.855(3)	5.5(6)
H7	0.270(4)	0.667(2)	0.696(3)	5.1(6)
H8	0.259(3)	0.635(2)	0.465(2)	3.6(5)

Table III. Atomic Coordinates for 2,3-Dinitronaphthalene.

a) Biodynamics Institute.

b) Department of Chemistry.

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24. a) Notice that nitrous acid is a by-product. Nitrous acid is in equilibrium with dinitrogen trioxide and water. N_2O_4 disproportionates to nitric and nitrous acids in the presence of water. b) The nitrations of fluoranthene[22] and anthracene[12,23] with NO_2 in CH_2Cl_2 also follow a different mechanism in the presence of small amounts of water.

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Chapter IV. Supplementary Material.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N1	1.203(2)	C3	C4	1.351(2)
O2	N1	1.229(2)	C4	C10	1.415(2)
O3	N2	1.196(2)	C5	C6	1.355(3)
O4	N2	1.234(2)	C5	C10	1.410(2)
N1	C2	1.461(2)	C6	C7	1.398(3)
N2	C3	1.461(2)	C7	C8	1.362(3)
C1	C2	1.361(2)	C8	C9	1.413(2)
C1	C9	1.407(2)	C9	C10	1.424(2)
C2	C3	1.406(2)			

Table I. Bond Distances Involving Nonhydrogen Atoms for 2,3-Dinitronaphthalene.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1	H1	0.94(2)	C6	H6	0.86(2)
C4	H4	0.94(2)	C7	H7	0.92(2)
C5	H5	1.01(2)	C8	H8	0.92(2)

Table II. Bond Distances Involving Hydrogen Atoms for 2,3-Dinitronaphthalene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	N1	O2	124.8(2)	C2	C3	C4	120.6(1)
O1	N1	C2	118.1(2)	C3	C4	C10	120.7(1)
O2	N1	C2	116.9(2)	C6	C5	C10	120.2(2)
O3	N2	O4	123.1(2)	C5	C6	C7	121.0(2)
O3	N2	C3	119.4(2)	C6	C7	C8	120.7(2)
O4	N2	C3	117.2(2)	C7	C8	C9	120.1(2)
C2	C1	C9	120.5(1)	C1	C9	C8	122.2(1)
N1	C2	C1	118.3(2)	C1	C9	C10	119.0(1)
N1	C2	C3	120.9(1)	C8	C9	C10	118.8(2)
C1	C2	C3	120.5(1)	C4	C10	C5	122.2(2)
N2	C3	C2	121.1(2)	C4	C10	C9	118.7(1)
N2	C3	C4	117.9(1)	C5	C10	C9	119.1(2)

Table III. Bond Angles in Degrees Involving Nonhydrogen Atoms for 2,3-Dinitronaphthalene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	H1	120(1)	C5	C6	H6	122(1)
C9	C1	H1	120(1)	C7	C6	H6	117(1)
C3	C4	H4	120(1)	C6	C7	H7	122(1)
C10	C4	H4	119(1)	C8	C7	H7	117(1)
C6	C5	H5	124(1)	C7	C8	H8	120(1)
C10	C5	H5	116(1)	C9	C8	H8	120(1)

Table IV. Bond Angles in Degrees Involving Hydrogen Atoms for 2,3-Dinitronaphthalene.

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.206(3)	0.109(2)	0.038(1)	-0.034(2)	0.009(1)	0.008(1)
O2	0.109(2)	0.083(1)	0.070(1)	-0.011(1)	-0.027(1)	-0.022(1)
O3	0.173(2)	0.048(1)	0.123(2)	-0.032(1)	0.021(2)	0.001(1)
O4	0.101(2)	0.074(1)	0.090(1)	0.018(1)	0.001(1)	-0.029(1)
N1	0.085(2)	0.062(1)	0.043(1)	0.000(1)	-0.005(1)	-0.006(1)
N2	0.089(2)	0.044(1)	0.067(1)	-0.001(1)	-0.004(1)	-0.006(1)
C1	0.048(1)	0.041(1)	0.036(1)	0.000(1)	-0.000(1)	0.008(1)
C2	0.046(1)	0.047(1)	0.032(1)	-0.002(1)	0.000(1)	-0.000(1)
C3	0.046(1)	0.032(1)	0.045(1)	-0.002(1)	0.001(1)	-0.001(1)
C4	0.049(1)	0.037(1)	0.045(1)	0.000(1)	0.001(1)	0.011(1)
C5	0.055(1)	0.066(2)	0.040(1)	-0.001(1)	0.002(1)	-0.000(1)
C6	0.064(2)	0.074(2)	0.047(1)	-0.001(1)	0.003(1)	-0.020(1)
C7	0.057(2)	0.050(1)	0.072(2)	-0.003(1)	0.005(1)	-0.022(1)
C8	0.047(1)	0.037(1)	0.062(2)	-0.000(1)	0.004(1)	-0.000(1)
C9	0.034(1)	0.035(1)	0.043(1)	0.000(1)	0.0015(9)	0.001(1)
C10	0.039(1)	0.045(1)	0.034(1)	-0.000(1)	0.0019(9)	0.002(1)

Table V. Anisotropic Thermal Parameters for 2,3-Dinitronaphthalene.

APPENDIX

This Appendix describes:

(1) The calibration of the nitrogen dioxide solutions.

(2) the determination of the molar relative response factors of nitro-PAH towards the flame ignition detector.

(3) Selected NMR experiments conducted on some of the reaction products that, due to the emphasis on journal space economy, were not included at the time the preceeding manuscripts were submitted for publication. Some of these experiments will form part of a future publication on the assessment of the mutagenic properties of nitrofluoranthenes conducted in collaboration with Dr. Barbara Shane of the Institute for Environmental Studies of Louisiana State University. All spectra were recorded on the Bruker AM 400 NMR spectrometer with the exception of the ^{1}H-^{1}H COSY 45 of 1-phenyl-4-nitronaphthalene which was recorded on the AC 200.

(4) Implementation of a selective version of the Insensitive Nuclei Enhanced by Polarization Transfer NMR technique (selective INEPT, also called INAPT). The spectra were recorded on the AM 400 NMR spectrometer.

(5) FTIR spectra of 1,2- and 1,3-dinitrofluoranthene; and of cis- and trans- 9,10-dinitro,9,10-dihydroanthracene.

(6) X-Ray crystallographic data of 1-phenyl-4-nitronaphthalene.

Calibration of Nitrogen Dioxide Solutions. *Caution!* Nitrogen dioxide is a pernicious gas[1] that must be handled in a good hood. A simple way of determining the concentrations of NO_2 and N_2O_4 is based on Beer's Law. The only absorbing species at 410 nm is nitrogen dioxide, and the concentrations of NO_2 and its dimer at equilibrium can be calculated from the dimer dissociation constant[2] at 25 ^oC, which is 1.78×10^{-4} M in CCl_4. Careful attention was given to minimize headspaces. Known weights of NO_2 were transferred from a small bulb provided with a Teflon stopcock to volumetric flasks containing CCl_4. The amount of transferred NO_2 was determined by differential weighing. The absorbances at 410 nm of the solutions prepared this way were then measured. The measurements were conducted on a Hewlett Packard 8451A diode array spectrometer and a 1 cm path cell thermostated at 25 ^oC. A calibration plot is shown in Fig 1. A good straight line (R^2=0.998) is observed as well as a small deviation from the origin, the latter most probably caused by minor losses of NO_2 during transfer.

Molar Relative Response Factors to the Flame Ignition Detector. The molar relative response factors (molar-RRF) were determined by preparing two solutions containing different amounts of the PAH, the mononitro-PAH and the dinitro-PAH. Each solution was then analysed at least by

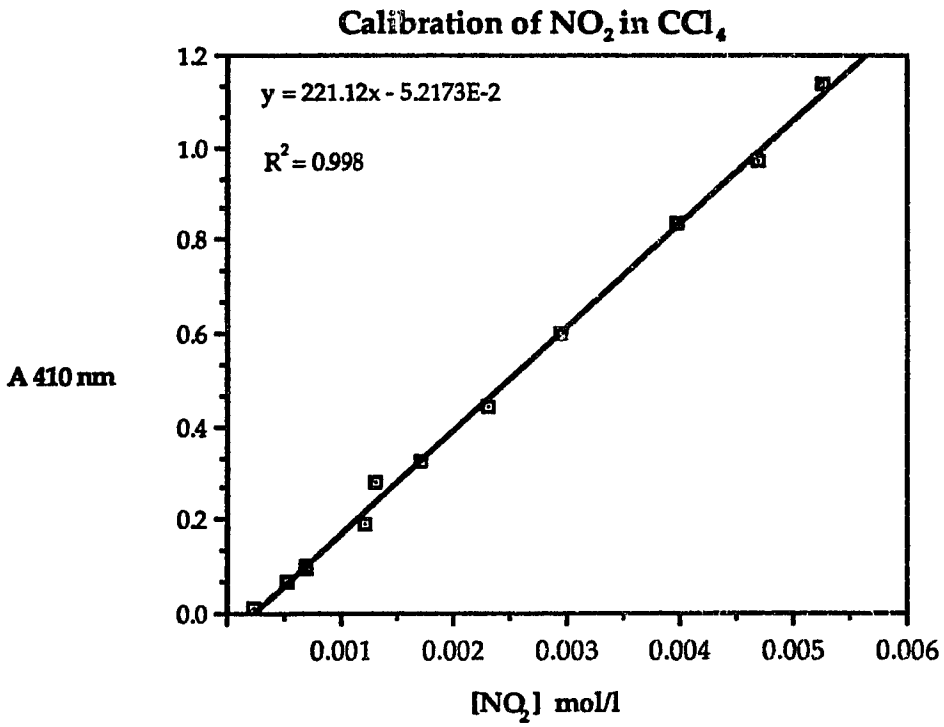


Figure 1. Calibration Plot for NO_2/N_2O_4 in CCl_4.

duplicate and the average was determined. The molar-RRF of the naphthalene and fluoranthenes are shown in Table I.

Nuclear Overhauser Effect Experiments. All the nuclear Overhauser effect (NOE) experiments are shown as the difference of the irradiation and the control experiment. The control experiment is displayed below the difference spectrum for further reference. The difference spectra were obtained by subtracting the free induction decay signals (FID's) of the irradiation and control experiments. The difference obtained this way was Fourier-transformed with small line-broadening (equal to or lower than the digital resolution employed) to improve the inherent low signal-to-noise ratio of these experiments. The Fourier-transformed spectra were then phased. In some cases an effect known as Selective Population Transfer (SPT) was generated because of the efforts on making the saturation selective, that is, avoiding the saturation of other resonances near the resonance of choice. Although the SPT signals can be large and distracting, they can be easily recognized because they are antiphase signals that have zero integral. Furthermore, SPT is generated only on resonances that are J-coupled to the saturated resonance.

1,2-Dinitrofluoranthene (1,2-DNF). As shown in Fig 2b, irradiation of the downfield singlet of one of the

Compound	molar-RRF	
Naphthalene	1.00[a]	
1-Nitronaphthalene	0.66	
2-Nitronaphthalene	0.62	
dinitronaphthalenes	0.52	
Fluoranthene	1.00[b]	1.00[c]
Mononitrofluoranthenes	0.74	0.80
Dinitrofluoranthenes	0.57	0.49

(a) Column: 30 m DB-5 J&W 0.25 mm I.D. Temperature Program: Initial Temperature: 70 ^{o}C; Temperature Ramp: 10 ^{o}C/min; Final Temperature: 280 ^{o}C, hold. (b) Column: 55 m DB-17 J&W 0.25 mm I.D. Temperature Program: Initial Temperature: 200 ^{o}C, 5 min; Temperature Ramp: 5 ^{o}C/min; Final temperature: 300 ^{o}C, hold. (c) Column: 30 m DB-17 J&W 0.25 mm I.D. Initial Temperature: 180 ^{o}C; Temperature Ramp: 15 ^{o}C/min; Final Temperature: 280 ^{o}C, hold.

Table I. Molar Relative Response Factors to the Flame Ignition Detector for Naphthalenes and Fluoranthenes.

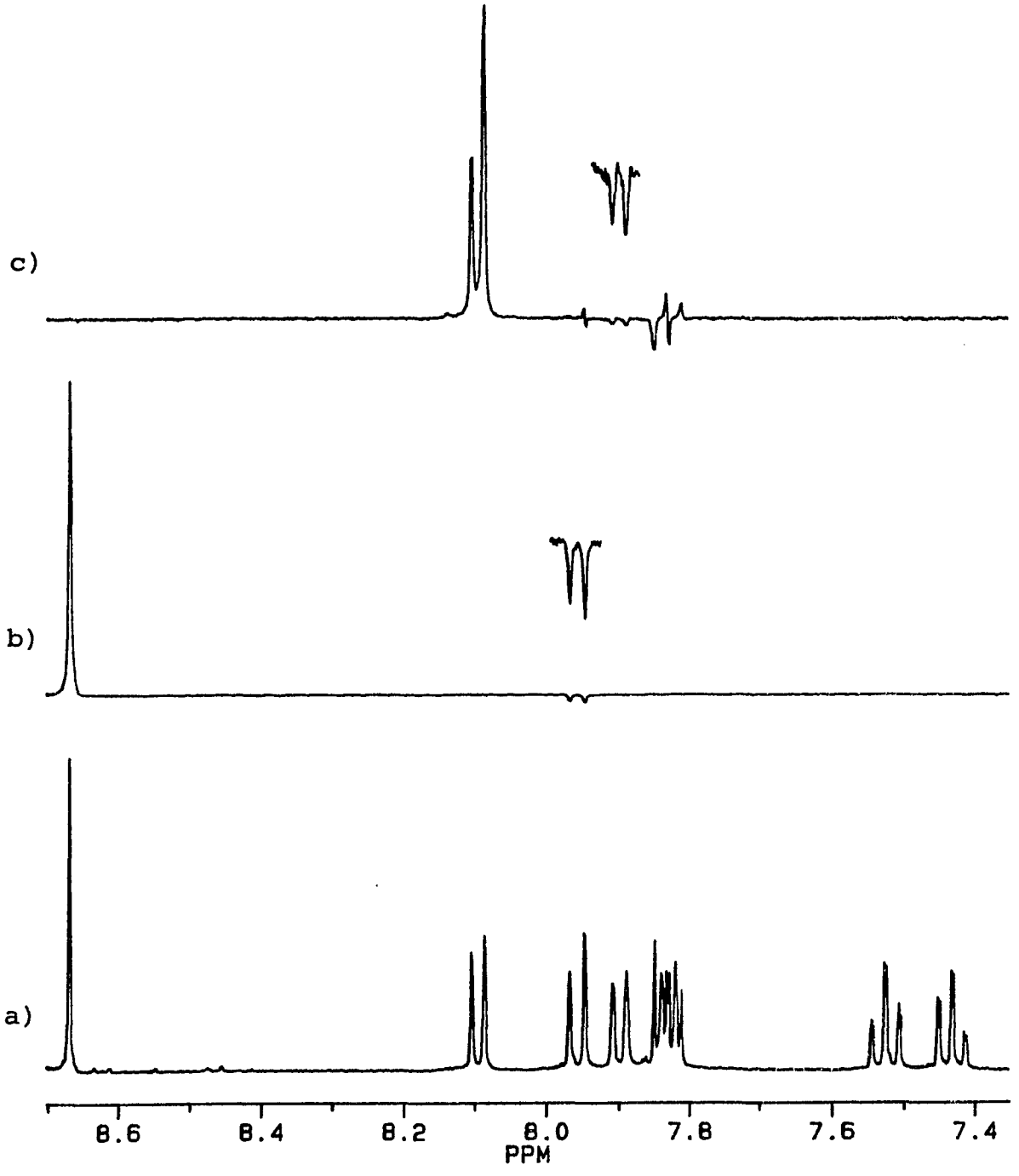


Figure 2. Nuclear Overhauser Experiments on 1,2-Dinitrofluoranthene. a) Control experiment. b) Saturation of H-3. c) Saturation of H-6.

dinitrofluoranthenes isolated from the nitration mixture of fluoranthene (Chapters I and II) causes NOE on a doublet member of the 3-spin subspectrum (see ^{1}H-^{1}H COSY 45 experiment in Fig 7). This information leads to the assignment of the substitution pattern as 1,2-DNF, excluding the alternative assignments 1,3-DNF and 2,3-DNF. 1,3-Dinitrofluoranthene is not expected to show (and experimentally does not show any) detectable NOE upon irradiation of its downfield singlet (in this case H2) because the neighboring protons are too far from the proton giving rise to the downfield resonance. Similarly, upon irradiation of its downfield singlet (in this case H1) 2,3-DNF would have been expected to show NOE on a doublet of its four-spin subspectrum (H10). Thus, the resonance where the NOE is observed upon irradiation of the downfield singlet (H3) in 1,2-DNF, is H-4. Similarly, irradiation of the other doublet of the 3-spin subspectrum of 1,2-DNF (H6) causes NOE on a doublet of its 4-spin subspectrum (H7), as shown in Fig 2c, and provides the assignment of H7 and H10. Complete assignment was made possible by combining this information with that of a ^{1}H-^{1}H-COSY 45 experiment (vide infra).

8-Nitrofluoranthene (8NF). A similar experiment was conducted on 8NF. The downfield doublet is assigned to H7 due to its characteristic small meta coupling. Irradiation of H8 results on NOE on H6, as observed in Fig

3b. Complete assignment was made possible by combining this information with that of a 1H-1H-COSY 45 experiment (vide infra).

^{1}H-^{1}H-COSY 45 Experiments. COSY spectra were obtained by using the 90°-D2-t1-45°-FID pulse sequence, employing the COSYLR.AUR automation program provided with the Bruker software, and were symmetrized along the diagonal. Other parameters were set as follows:
1NF: D2=0.125 s.; data matrix of 512x512 data points; sixteen transients for each 256 t1 increments.
7NF: D2=0.125 s.; data matrix of 1024x1024 data points; thirtytwo transients for each 512 t1 increments.
8NF: D2=0.125 s.; data matrix of 512x512 data points; thirtytwo transients for each 256 t1 increments.
1,2DNF: D2=0.125 s.; data matrix of 256x256 data points; thirtytwo transients for each 128 t1 values.

The ^{1}H-NMR spectra of mononitrofluoranthenes have been studied in some detail by Paputta-Peck et al[3] and Svendsen et al.[4] The assignments of the 1H-NMR resonances are for the most part incomplete with some disagreements. We have worked with dilute solutions (10-15 mM) to avoid association of the test compounds and, therefore, changes in chemical shifts as a fuction of concentration. Our results are consistent with those of Paputta-Peck et al and provide further assignments which were made possible

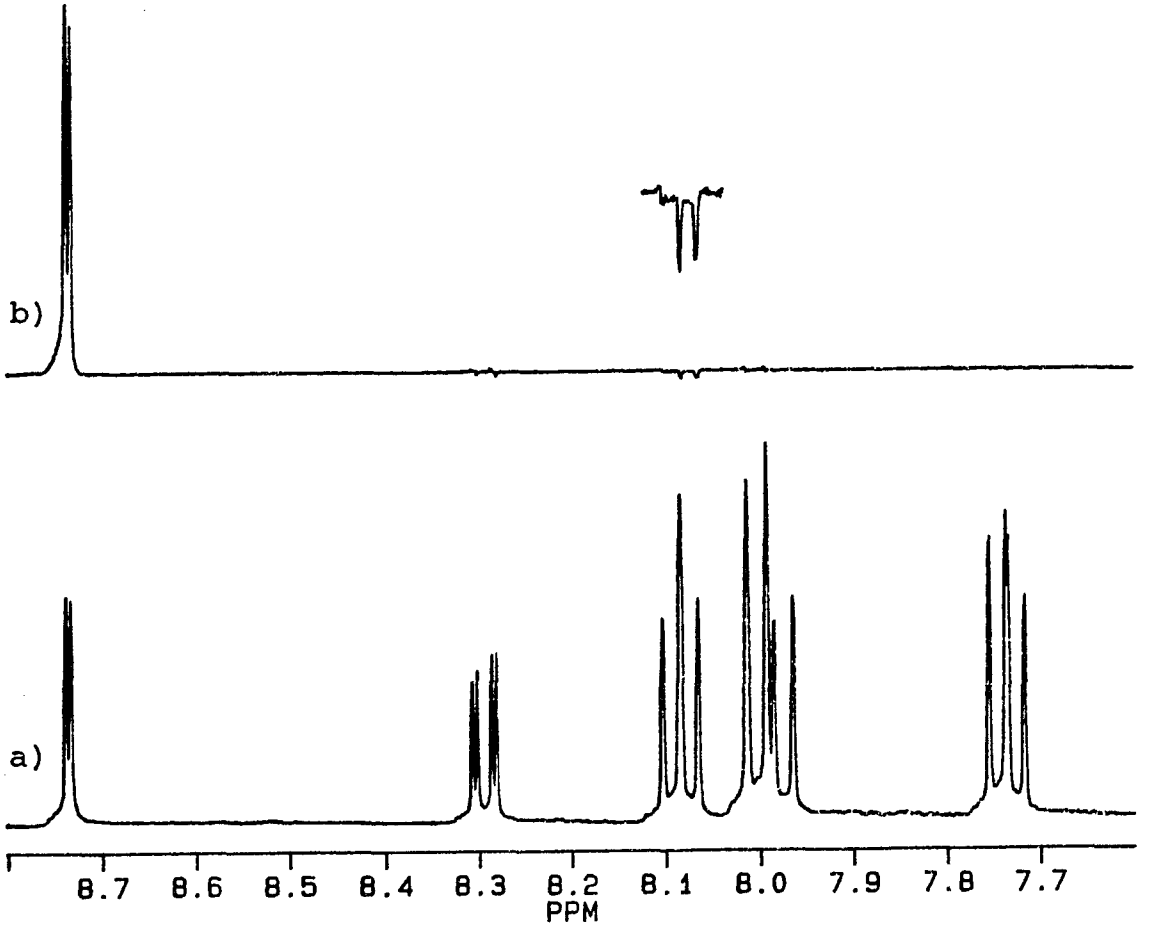


Figure 3. Nuclear Overhauser Experiment on 8-Nitrofluoranthene. a) Control experiment. b) Saturation of H-7.

by using the combined information of NOE and ^1H-^1H COSY 45 experiments. However, we were unable to converge to the chemical shifts reported by Svendsen et al even by increasing the monofluoranthenes concentration. In fact, a ten-fold increase in concentration only produced a 0.01-0.02 ppm chemical shift difference, which cannot account for the major differences with the results reported by Svendsen et al.

1-Nitrofluoranthene (1NF). The ^1H-^1H COSY 45 experiment of 1NF (Fig 4) reveals the presence of a two-spin, a three-spin and a four-spin subspectrum. The further downfield member of the two-spin subspectrum (8.21 ppm) is assigned as H2 due to the deshielding effect caused by the presence of the NO_2 substituent in the adjacent position. Consequently, H3 is assigned as the other member of the two-spin subspectrum (7.91 ppm). Similarly, the furthest downfield member of the four-spin subspectrum is assigned as H10 (8.49 ppm), and the broad doublet at 7.89 ppm as H7. Selective decoupling of H10 caused the collapse of the multiplet centred at 7.43 ppm to almost a doublet, providing the assignment of the latter as H9. Consequently, the remaining member of the four-spin subspectrum is assigned as H8 (multiplet centered at 7.48 ppm). The member of the three-spin subspectrum at 7.72 ppm is assigned as H5 due to its characteristic couplings to two nonequivalent ortho

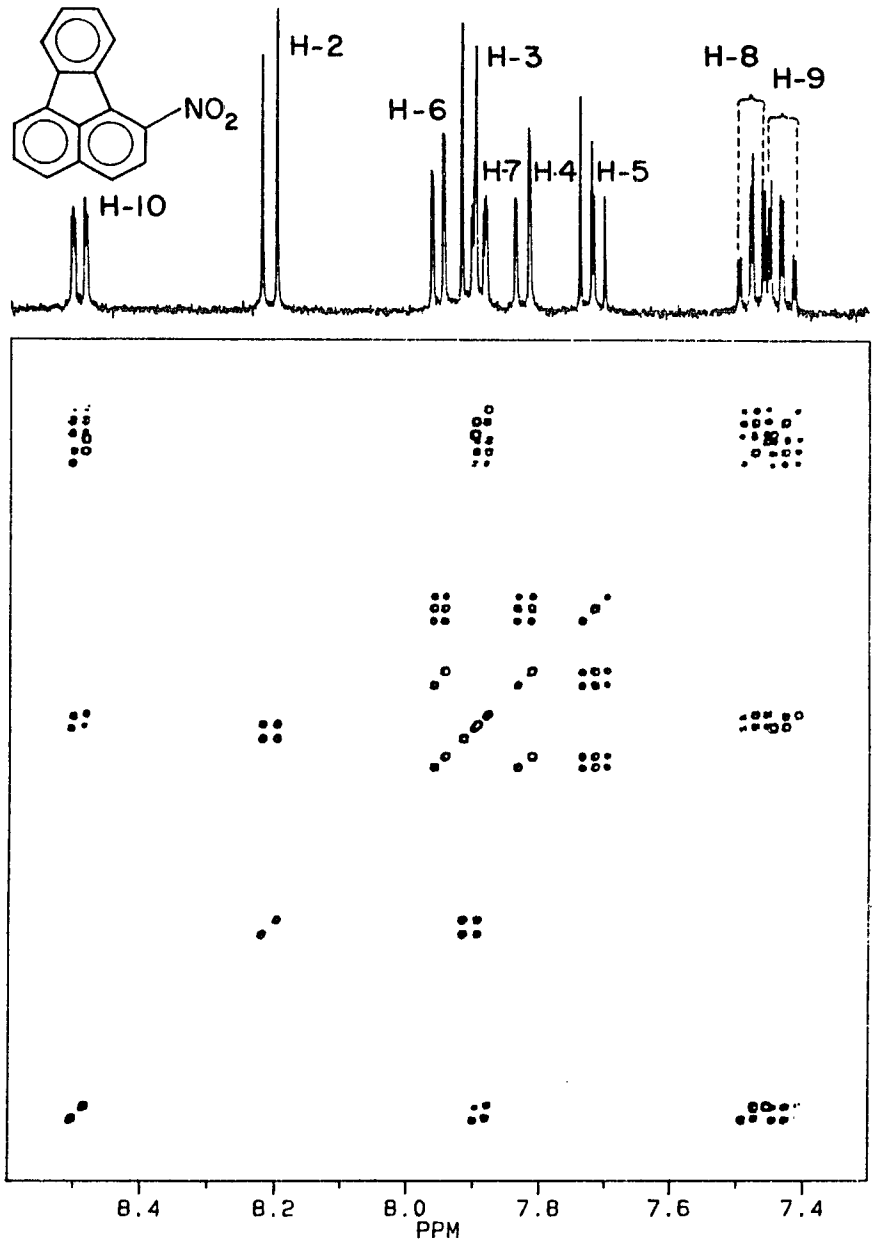


Figure 4. ^{1}H-^{1}H COSY 45 Spectrum of 1-Nitrofluoranthene.

protons. H4 (7.83 ppm) and H6 (7.95 ppm) are assigned by comparison to the assignments of fluoranthene.[6]

7-Nitrofluoranthene (7NF). The ^{1}H-^{1}H COSY 45 experiment of 7NF (Fig 5) reveals the presence of three three-spin subspectra. The furthest downfield doublet (8.68 ppm) is assigned as H6 because of the deshielding effect caused by the presence of the nitro group in the same "bay". The member of the subspectrum at 7.76 ppm is assigned as H5 due to its characteristic couplings to two nonequivalent ortho protons. Consequently, the remaining member of this subspectrum is assigned as H4 (8.03 ppm). Similarly, the signals centered at 8.22 ppm, 7.54 ppm, and 8.10 ppm are assigned as H8, H9, and H10, respectively. The multiplet centered at 7.72 ppm is assigned as H2 due to its characteristic couplings to two nonequivalent protons. The doublet at 7.99 ppm is assigned as H3 due to the crosspeaks indicative of small couplings. Consequently, the remaining member of this subspectrum is assigned as H1 (8.08 ppm).

8-Nitrofluoranthene (8NF). The ^{1}H-^{1}H COSY 45 experiment of 8NF (Fig 6) also reveals the presence of three three-spin subspectra. The furthest downfield doublet (8.76 ppm) is assigned as H7 because of the deshielding effect caused by the presence of the NO2 substituent in the adjacent position and the presence of only small couplings characteristic meta and para

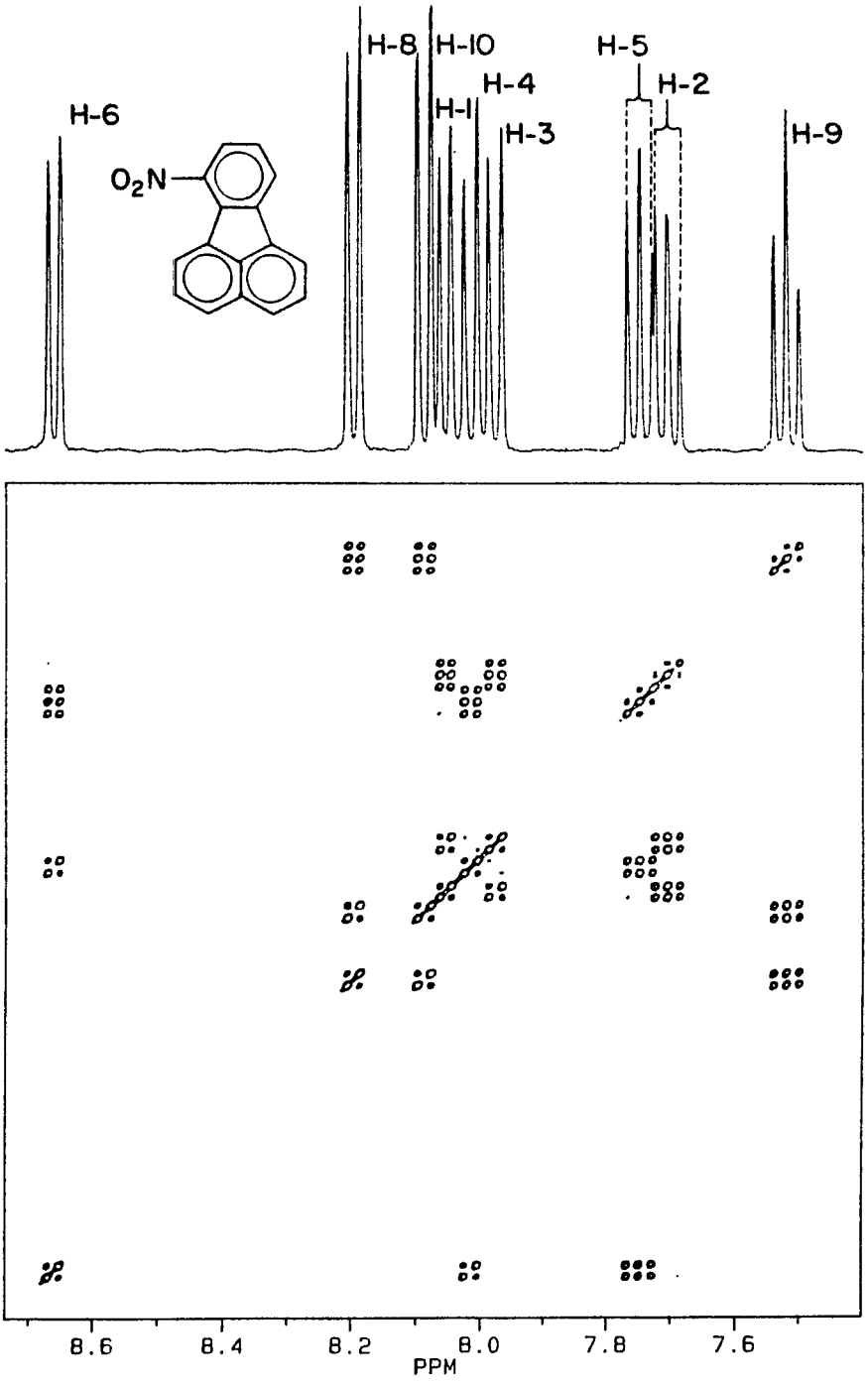


Figure 5. ^{1}H-^{1}H COSY 45 Spectrum of 7-Nitrofluoranthene.

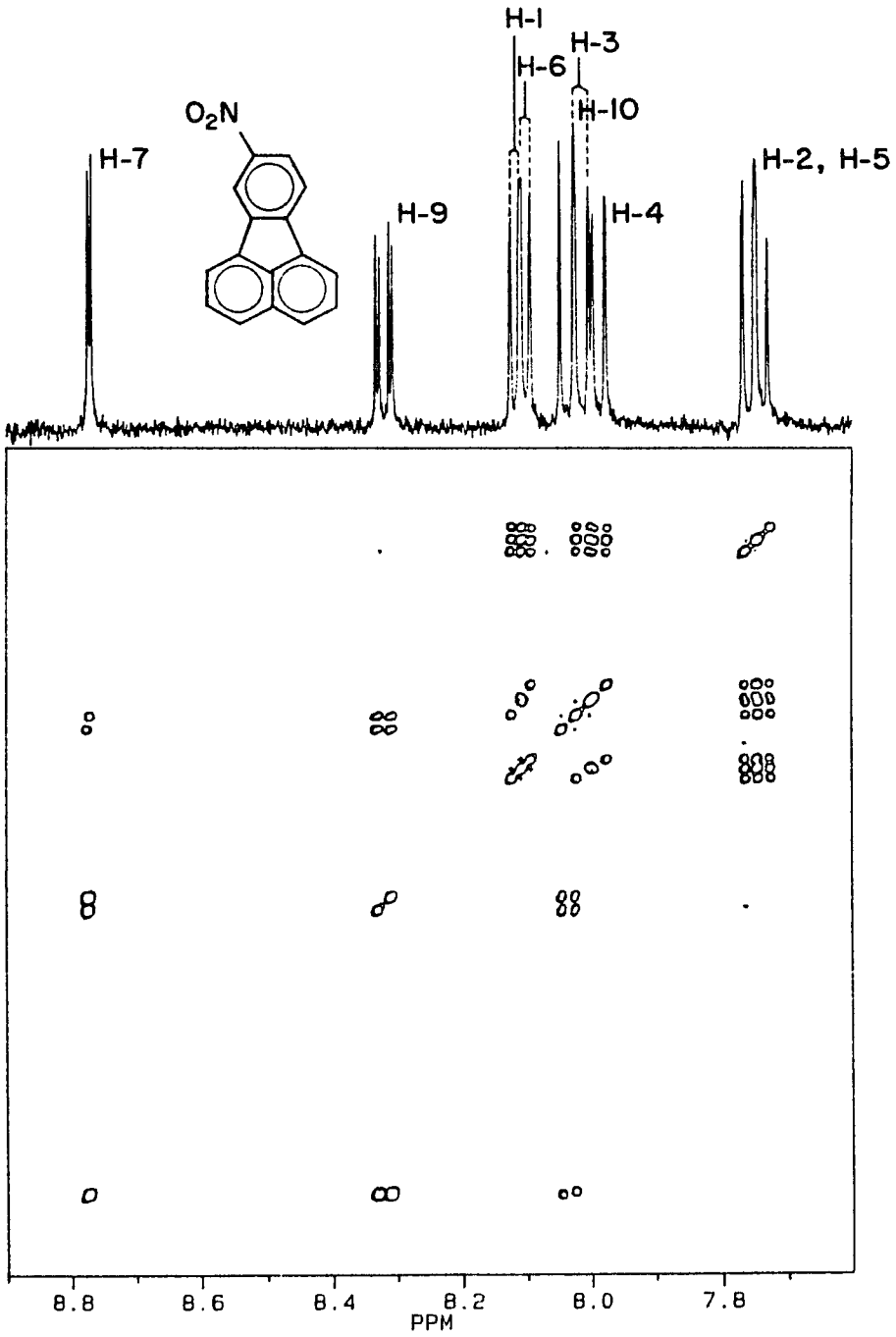


Figure 6. ^{1}H-^{1}H COSY 45 Spectrum of 8-Nitrofluoranthene.

couplings. The member of the subspectrum at 8.31 ppm is assigned as H9 due to its characteristic couplings to two nonequivalent protons (ortho and meta). Consequently, the remaining member of this subspectrum is assigned as H10 (8.03 ppm). A nuclear Overhauser effect experiment revealed the enhancement of the doublet at 8.09 ppm upon selective irradiation of H7, providing its assignment as H6. Consequently, the doublet at 7.98 ppm is assigned as H4, and the doublet-of-doublets at 7.75 ppm as H5 (almost perfectly superimposed to H2). H1 (8.11 ppm) and H3 (8.01 ppm) are assigned by comparison to the assignments of fluoranthene.[6]

1,2-Dinitrofluoranthene. Some assignments on the ^{1}H-NMR spectrum of 1,2DNF have been reported by Zielinska et al.[5] Our results provide a complete assignment and reveal that the signals for four protons have been previously misassigned.

The ^{1}H-^{1}H COSY experiment of 1,2DNF (Fig 7) reveals the presence of a singlet, a three-spin, and a four-spin subspectrum. The positions of the nitro groups were stablished by a nuclear Overhauser effect experiment that revealed the enhancement of the doublet at 7.96 ppm (H4) upon selective irradiation of the downfield singlet (H3). Consequently, the doublet-of-doublets at 7.83 ppm and the doublet at 8.09 ppm were assigned as H5 and H6, respectively. A nuclear Overhauser effect experiment

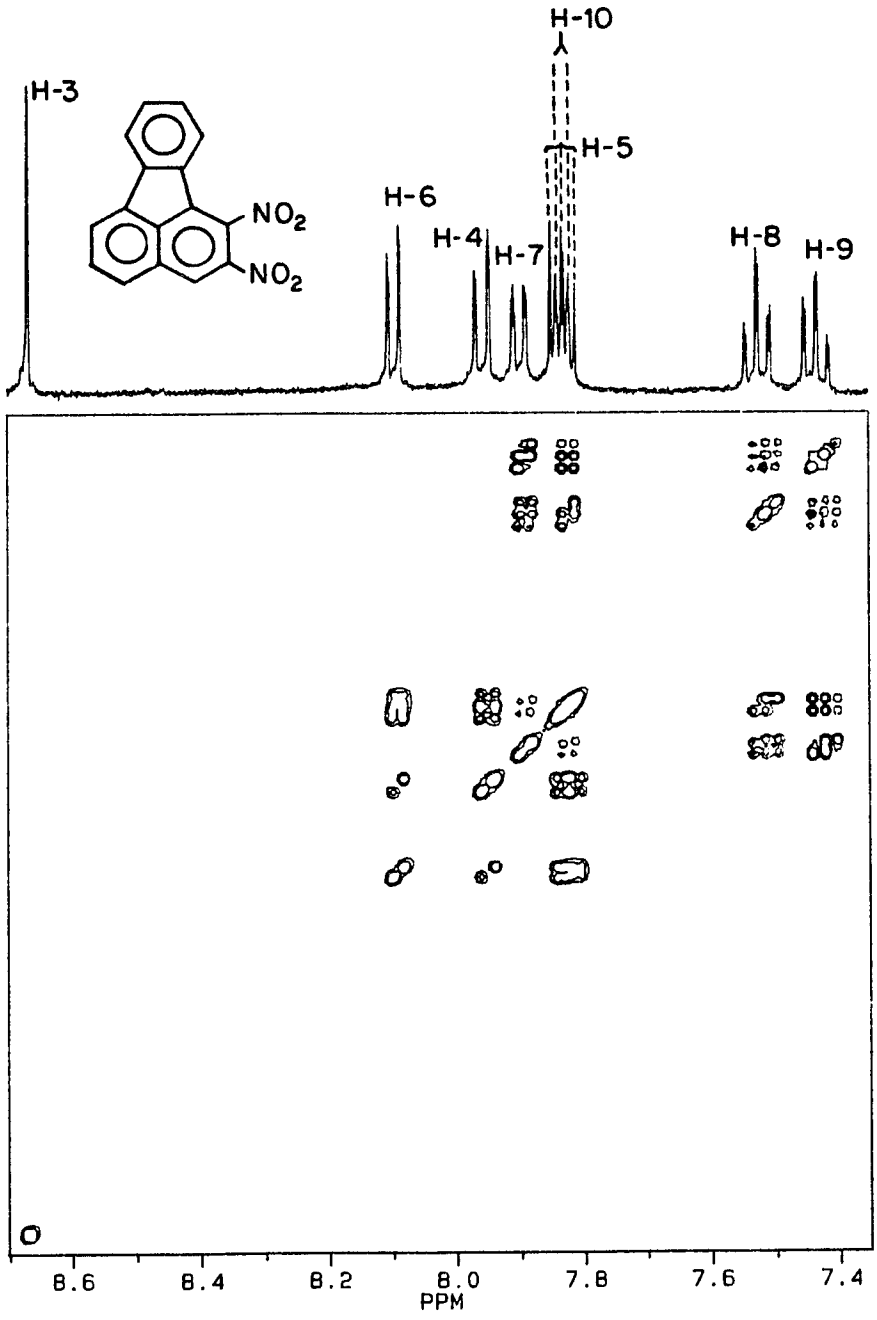


Figure 7. ^{1}H-^{1}H COSY 45 Spectrum of 1,2-Dinitrofluoranthene.

revealed the enhancement of the doublet at 7.90 ppm upon selective irradiation of H6, providing its assignment as H7. Consequently, the doublet at 7.83 ppm is assigned as H10. Selective decoupling of H7 caused the collapse of the multiplet centered at 7.52 ppm to almost a doublet, providing the assignment of the latter as H8. Consequently, the multiplet centred at 7.44 ppm is assigned as H9. Notice that the less usual disposition of the chemical shifts of H7 and H10 is indicative of an out-of-plane orientation of the nitro group in position one, as revealed by a single crystal X-ray study.[7]

1-Phenyl-4-nitronaphtahlene. During the course of the studies on the mutagenicity of the nitrofluoranthenes, 1-phenyl-4-nitronaphthalene was synthesized as a nonplanar analog of 3-nitrofluoranthene. The synthetic methodology employed was essentially the same as with the fluoranthenes (Chapters I and II): 6 mL of an NO2/N2O4 solution (0.14 M N(IV), CCl_4) were added to 2 mL of a 1-phenylnaphthalene solution (0.16 M, CCl_4). The solvent was thoroughly purged with argon. The yield of 1-phenyl-4-nitronaphthalene was higher than 90% (GC) with small amounts of another mononitro-isomer and of dinitro-isomers. The 1-phenyl-4-nitronaphthalene was purified by column chromatography on silica gel, using hexane:methylene chloride mixtures. The ^1H-^1H COSY 45 spectrum of 1-phenyl-4-nitronaphthalene (Fig 8, recorded

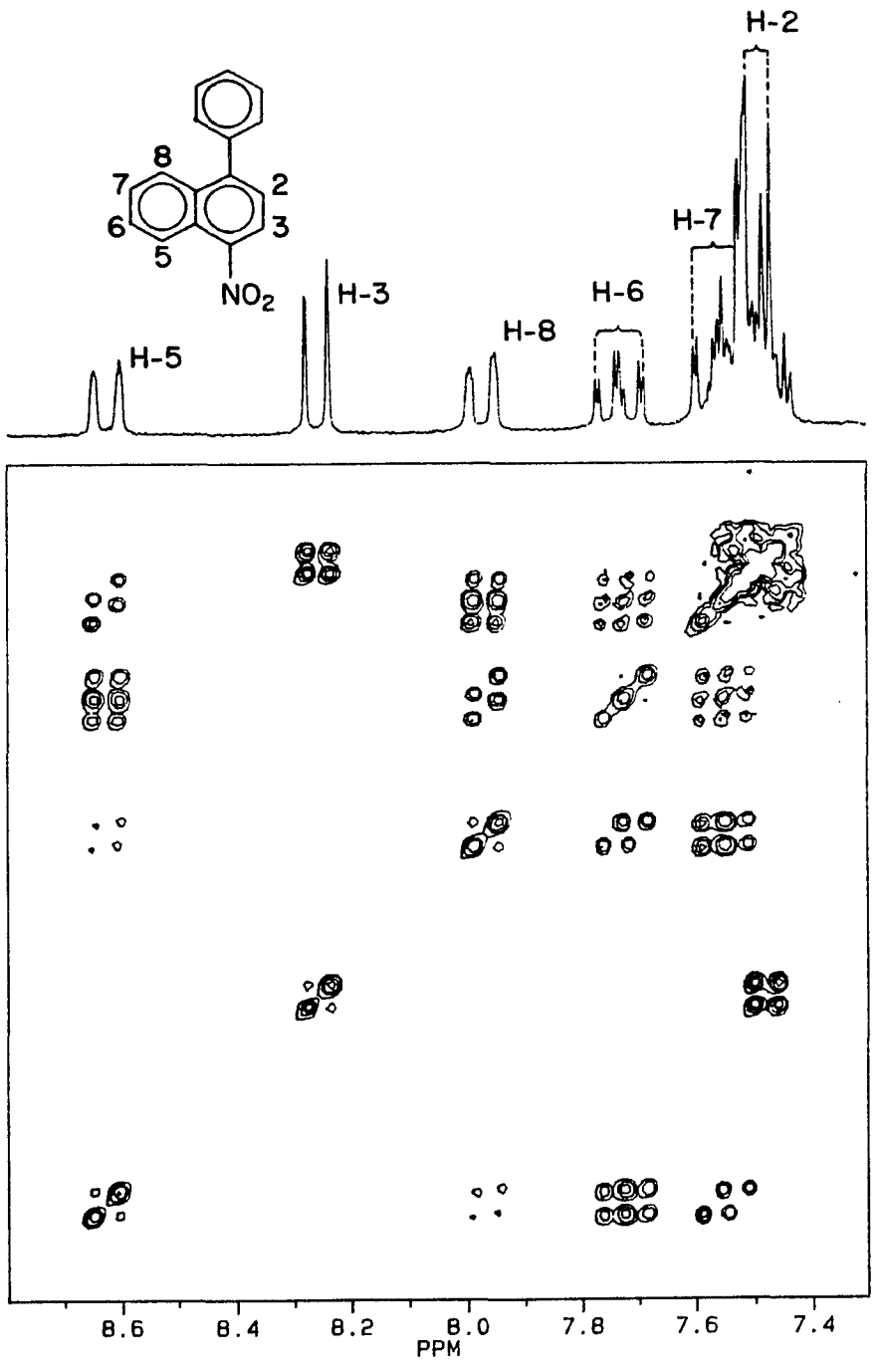
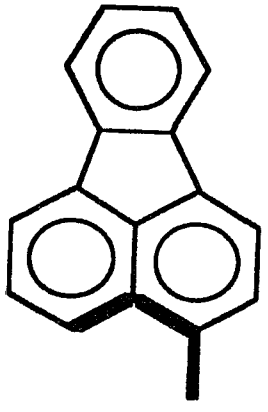


Figure 8. ^{1}H-^{1}H COSY 45 Spectrum of 1-Phenyl-4-nitronaphthlene.

with a data matrix of 256x256 data points; D2=0 s.; 16 transients for 128 t1 values) reveals the presence of a two-spin, a four-spin, and a tightly coupled five spin subspectrum. The position of the nitro group was stablished by inspection of characteristic couplings and chemical shifts of the protons near the site of substitution (e.g. ruling out the posibility of substitution at site-2, site-3, the other ring of the naphthalene moiety or the phenyl substituent). The further downfield member of the four-spin subspectrum (8.62 ppm) is assigned as H5 due to the deshielding effect caused by the presence of the nitro substituent in the peri position. Consequently, the broad doublet at 7.97 ppm, and the multiplets at 7.72 ppm and 7.55 ppm are assigned as H8, H6 and H7, respectively. Similarly, the further downfield member of the two-spin subspectrum (8.26 ppm) is assigned as H3. Consequently, the doublet at 7.50 ppm is assigned as H2. The tightly coupled five-spin subspectrum (7.42-7.57 ppm) consists of H2' to H6'.

Implementation of a Selective Version of the Insensitive Nuclei Enhanced by Polarization Transfer Technique (selective INEPT, also called INAPT). The selective INEPT (INAPT) is a very sensitive technique for the assignment of quaternary carbons and for the indirect assignment of proton resonances in complicated spectra commonly found aromatic systems. This ^{13}C-observed

technique is based on the selective irradiation of a proton resonance, which transfers its polarization to coupled carbon atoms. The flexibility of the program (vide infra) allows for optimization to observe polarization transfer to carbon atoms located either one or three bonds from the irradiated proton, the latter is considered the more powerful application of the technique and was also exploited here. This technique was added to the microprogram library of the NR 100, AC 200, and AM 400 spectrometers. The selective INEPT technique was implemented to help establish the substitution patterns in the dinitrofluoranthenes and to indirectly assign the proton spectra of both mono- and dinitrofluoranthene. However, the inefficient polarization transfer through the bonds in the fluoranthene moiety, apparently due to



coupling constants smaller than the expected, forced to use the program under conditions of substantial relaxation before starting acquisition, resulting in low signal-to-noise ratios. The appearance of signals due to polarization transfer via the usually small $^{2}J_{CH}$ couplings caused additional complications. This technique therefore was found unsatisfactory for the nitrofluoranthenes. Furthermore, the low solubility of dinitrofluoranthenes aggravated the problem. Despite the problems encountered with these applications, some of my colleagues successfully applied this technique, particularly for the assignment of quaternary carbons and for indirect assignment of proton spectra in natural products. Thus, details of the implementation of the selective INEPT technique, and of the automation program INAPT.AUR (in the AM 400 spectrometer) and INAPT.AU (in the NT 200 and the NR 100 spectrometers) are provided below for the benefit of future users.

The pulse train and the corresponding phase program of the selective INEPT technique were published recently by Bax and his coworkers[8] (Fig 9). Both pulse train and phase program were translated into Bruker language. The problem of placing the first 180^{o} ^{13}C pulse of 0^{o} phase shift midway through the first selective 180^{o} ^{1}H pulse of 0^{o} phase shift was circumvented by cutting the ^{1}H pulse into two 90^{o} pulses of 0^{o} phase shift each and placing the

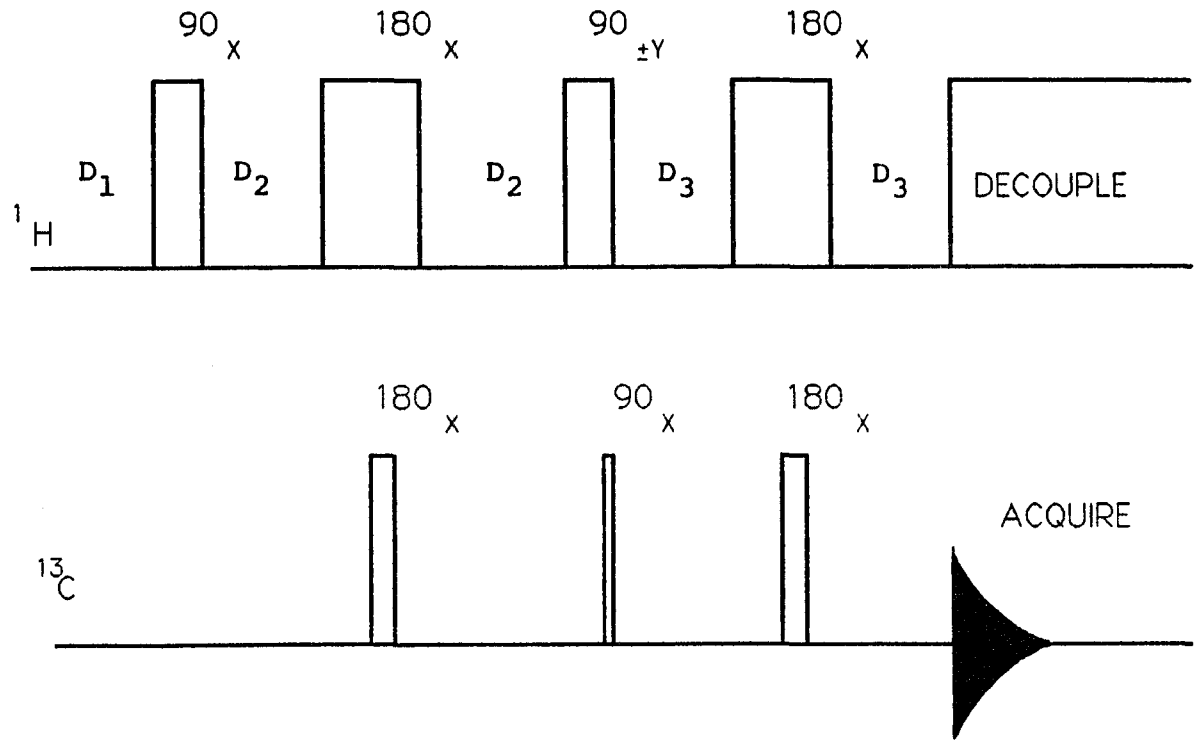


Figure 9. Selective INEPT pulse train proposed by Bax.

^{13}C pulse right after the first 90° ^{1}H pulse. The same strategy was used with the second 180° ^{13}C and ^{1}H pulses. Broad band (BB) decoupling was used with the NT 200 and the NR 100 spectrometers, while an alternative decoupling technique termed composite pulse decoupling (CPD) was used to provide ^{1}H decoupling with the AM 400 spectrometer. In order to avoid unnecesary relay wearout due to switching between the decoupler low (L) and high (H) power settings, especially during experiments requiring many accumulations, nonselective decoupling is done at the highest power available in the L decoupler settings (0L). This way, decoupling and the selective pulses are done in the L decoupler settings.

The dual probe (^{13}C-^{1}H) was used to conduct this experiment and thus the decoupler channel was employed to provide both nonselective decoupling and the selective proton pulses. The 90° pulse at 0L for CPD was measured the usual way, employing the DEC90.AUR microprogram (provided with the Bruker software) and benzene as test sample. For measuring the 90° soft pulses, dichloroacetic acid was used as test sample (observing the antiphase doublet of the carboxyl carbon, $^{2}J_{CH}$=2.4 Hz) and adding the duration of the variable pulse to the delay that follows it in the DEC90.AUR microprogram. Thus, satisfying the condition D2 = P1 + 1/2J.

The INAPT.AUR microprogram, the 90° decoupler pulse

at 0L, and some soft 90^{o} pulses of different field strengths are listed below.

INAPT.AUR

```
1 ZE
2 D1 S1 DO          ;D1 + AQ = ca. 2 sec
3 (P1 PH1 D2):D     ;Select appropiate P1 and S1 from chart
4 (P1 PH1):D        ;2D2 + 2P1 = 1/2J
5 P2 PH2
6 (P1 PH1 D2):D
7 (P1 PH3 D3):D (D4 P4 PH2)
                    ;2D3 + P1 = 1/2J; P4 - P1 = D4
8 (P1 PH1):D
9 P2 PH2
10 (P1 PH1):D (D3 S2)       ;S2 = 0L
11 GO=2 PH4 CPD
12 D2 DO
13 EXIT

PH1=BO
PH2=A0
PH3=B1 B3
PH4=R0 R2
```

The microprogram requires entry of the frequency

offset of the signal to be irradiated (O2), and $^3J_{CH}$ (J in the microprogram comments) is frequently estimated around 6 to 10 Hz, especially for aromatic systems. When using the CPD decopling mode, the program also requires the 90° decoupler pulse at OL to be entered as P9. When using the AC 200 or the NR 100 spectrometers replace CPD with BB in line 11. The conditions decribed in the microprogram comments are for polarization transfer from methine protons. For transfer from a methylene, or from a methyl, the delays 2D2 + 2P1 and 2D3 + P1 have to be set to 1/4J or 1/5J, respectively.

90° Decoupler pulses on the AM 400:

Power	Duration
0L	115 usec
40L	10.5 msec
41L	12.5 msec
45L	18.0 msec
48L	27.0 msec

90° Decoupler pulses on the AC 200:

Power	Duration
41L	11.0 msec

The choice of selective pulse duration is based on how close the signal to be irradiated is to other signals. The shorter the pulse, the stronger the field strength; therefore, when neighboring signals are in close proximity to the signal to be irradiated, longer pulses are to be used. However, when possible, the shorter pulses are preferred to avoid unnecessary relaxation prior to starting acquisition.

The efficiency of polarization transfer through the bonds shown in p. 169 was tested in 2-nitrofluoranthene which has a relatively high solubility. A ^{13}C-^{1}H correlation experiment (using the microprogram XHCORR.AUR) was performed to stablish the assignments of the methine carbons, as shown in Fig 10. The effects of the selective irradiation of protons H1, H3, and H5 are shown in Fig 11. Irradiation of H1 and H3 result in polarization transfer via $^{3}J_{CH}$ to a common quaternary carbon, identified as C15 (134.80 ppm). Some transfer is also observed via ^{2}JCH to C2 (148.54 ppm). Irradiation of H1, and of H3 also result in polarization transfer to C3 (123.72 ppm), and to C1 (113.79 ppm), respectively and as expected. Irradiation of H1 also results in polarization transfer to a third quaternary carbon, identified as C11 (137.94 ppm). Irradiation of H5 results in very efficient transfer to two quaternary carbons, identified as C14 and C16 (137.28 and 128.11 ppm, interchangeable). However, irradition of

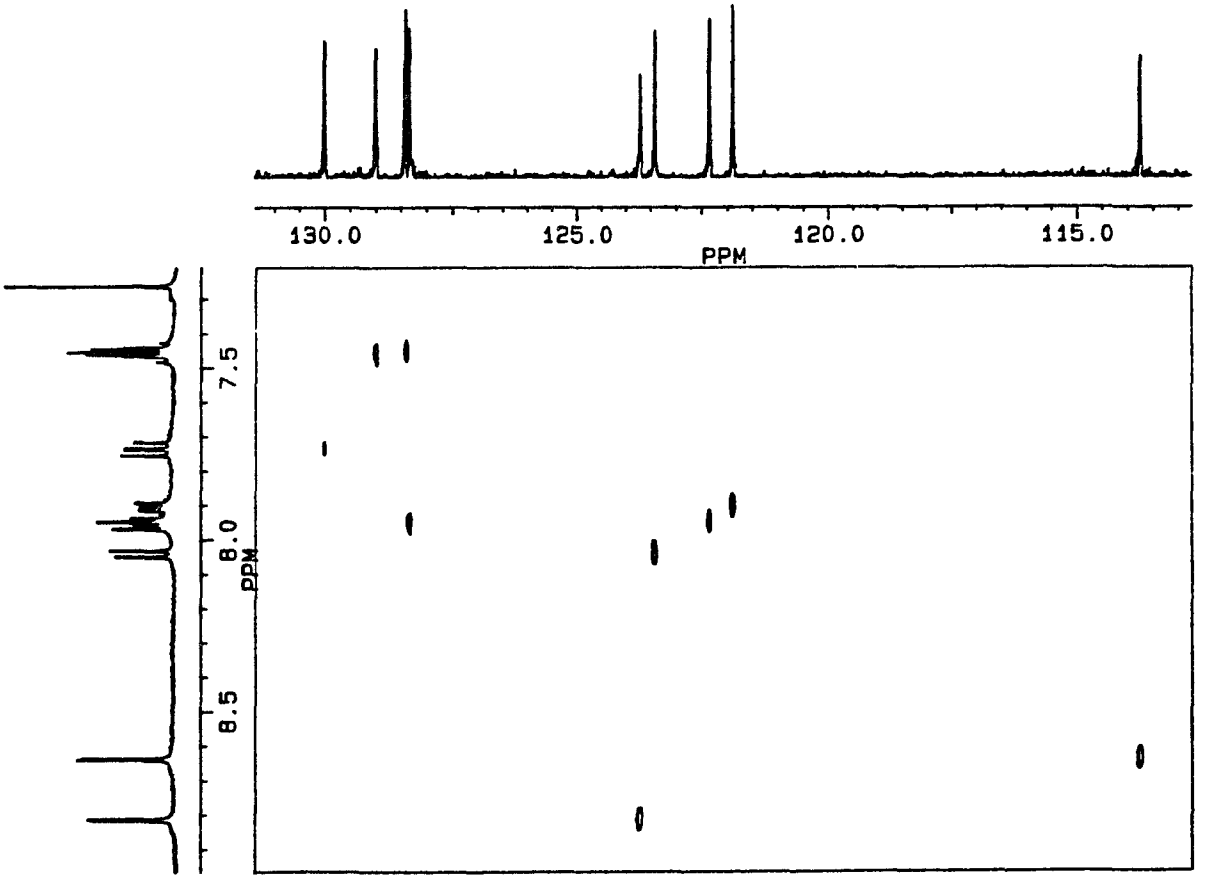


Figure 10. ^{13}C-^{1}H Correlation of 2-nitrofluoranthene.

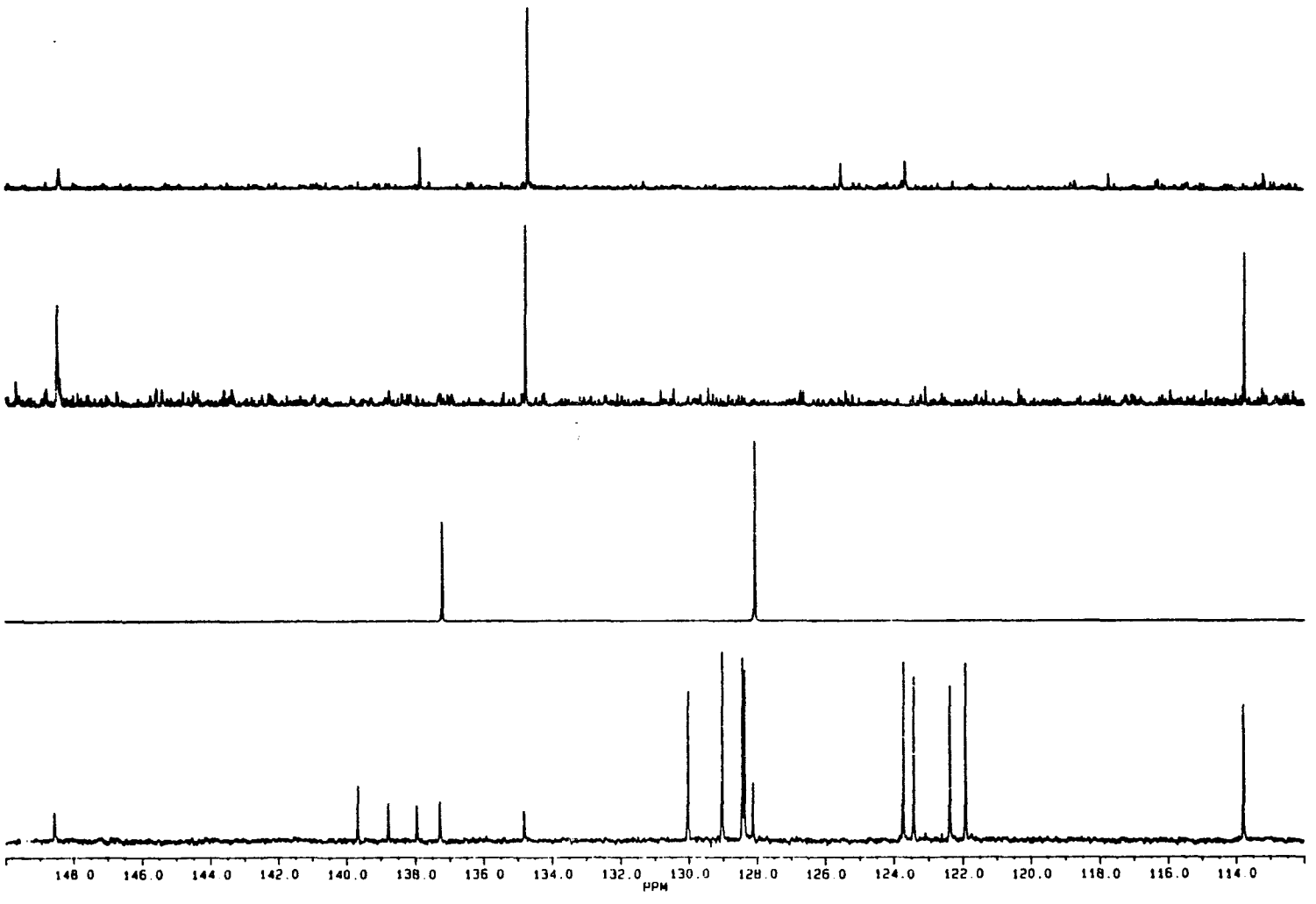


Figure 11. Selective INEPT Spectra of 2-Nitrofluoranthene. From top to bottom, irradiation of H1, H3, H5 and complete broad-band decoupled spectrum.

H3 does not result in polarization transfer to C4 (128.36 ppm) which was the transfer sought to exploit for future assignments. Other methine carbons assigned with the ^{13}C-^{1}H correlation are C5 (130.03 ppm), C9 (129.02 ppm), C8 (128.43 ppm), C6 (123.42 ppm), C10 (122.37 ppm), and C7 (121.91 ppm).

FTIR Spectra. FTIR spectra were recorded on a FTIR IBM/44 spectrometer using KBr pellets. The spectra of 1,2- and 1,3-dinitrofluoranthene, and of cis- and trans-9,10-dinitro-9,10-dihydroanthracene are shown in Figs 12 and 13, and Figs 14 and 15, respectively. The bands corresponding to asymmetric and symmetric stretching of the NO_2 group are the most noticeable features of the FTIR spectra. These bands are at 1563 cm^{-1} and 1351 cm^{-1} in 1,2-dinitrofluoranthene; at 1526 cm^{-1} and 1334 cm^{-1} in 1,3-dinitrofluoranthene; at 1563 cm^{-1} and 1351 cm^{-1} in cis-9,10-dinitro-9,10-dihydroanthracene; and at 1545 cm^{-1} and 1356 cm^{-1} in trans-9,10-dinitro-9,10-dihydroanthracene, respectively.

X-Ray Crystallographic Data for 1-Phenyl,4-nitronaphthalene. The position of substitution determined by NMR was confirmed by a single crystal X-ray analysis which also provided the spatial orientation of the phenyl and nitro substituents, as shown in Fig 16. X-ray data were collected using a crystal of dimensions

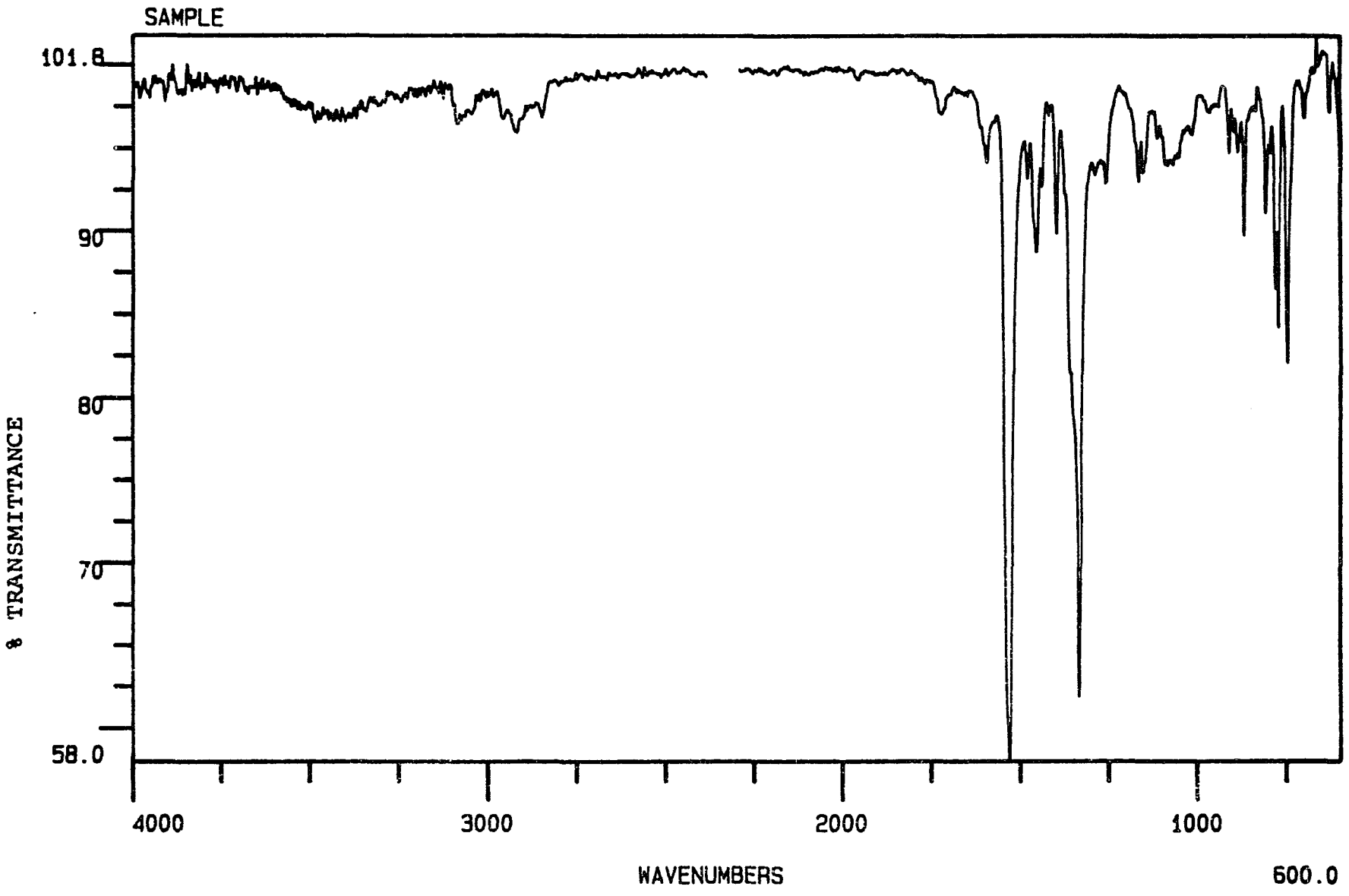


Figure 12. FTIR Spectrum of 1,2-Dinitrofluoranthene.

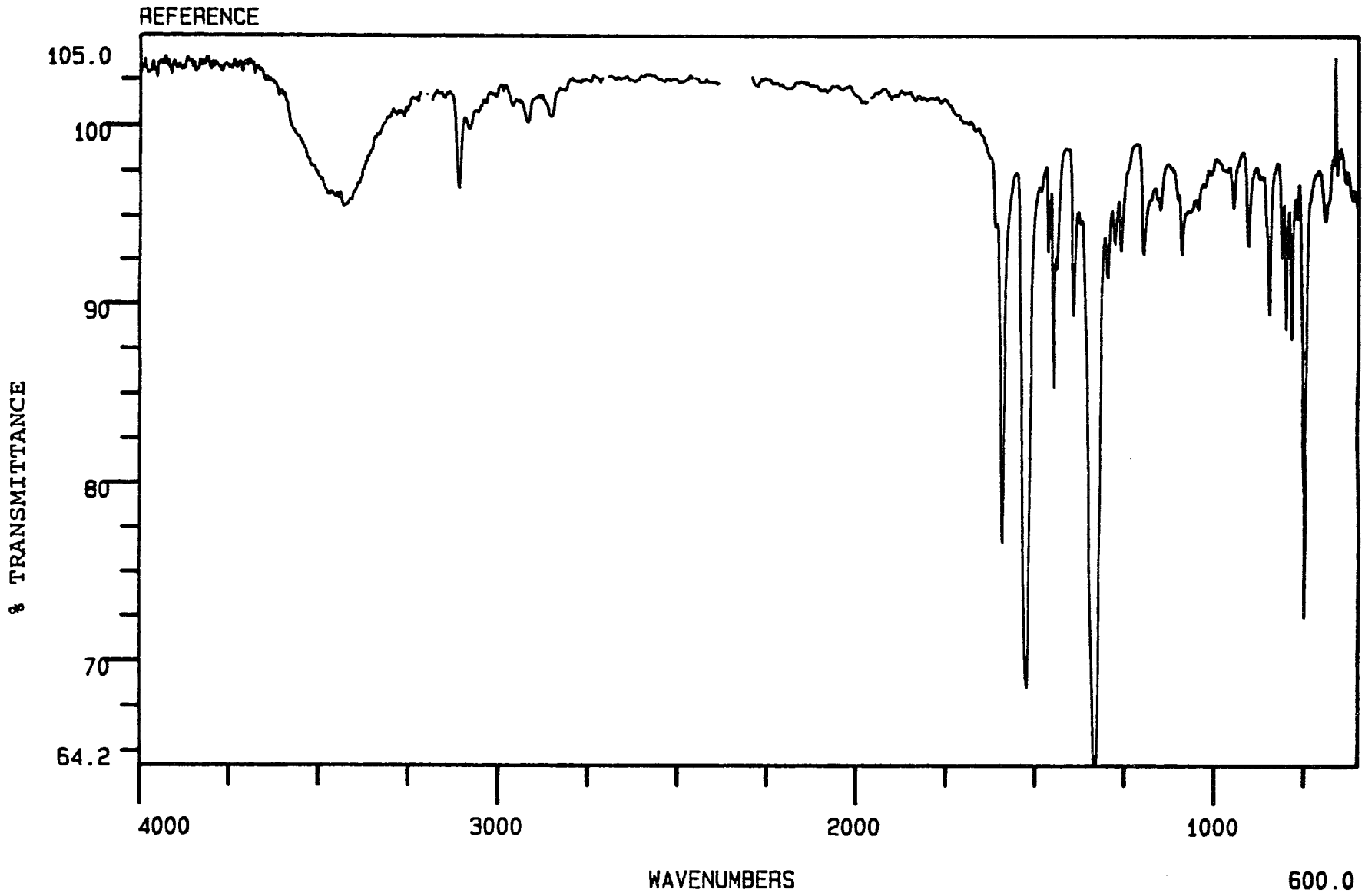


Figure 13. FTIR Spectrum of 1,3-Dinitrofluoranthene.

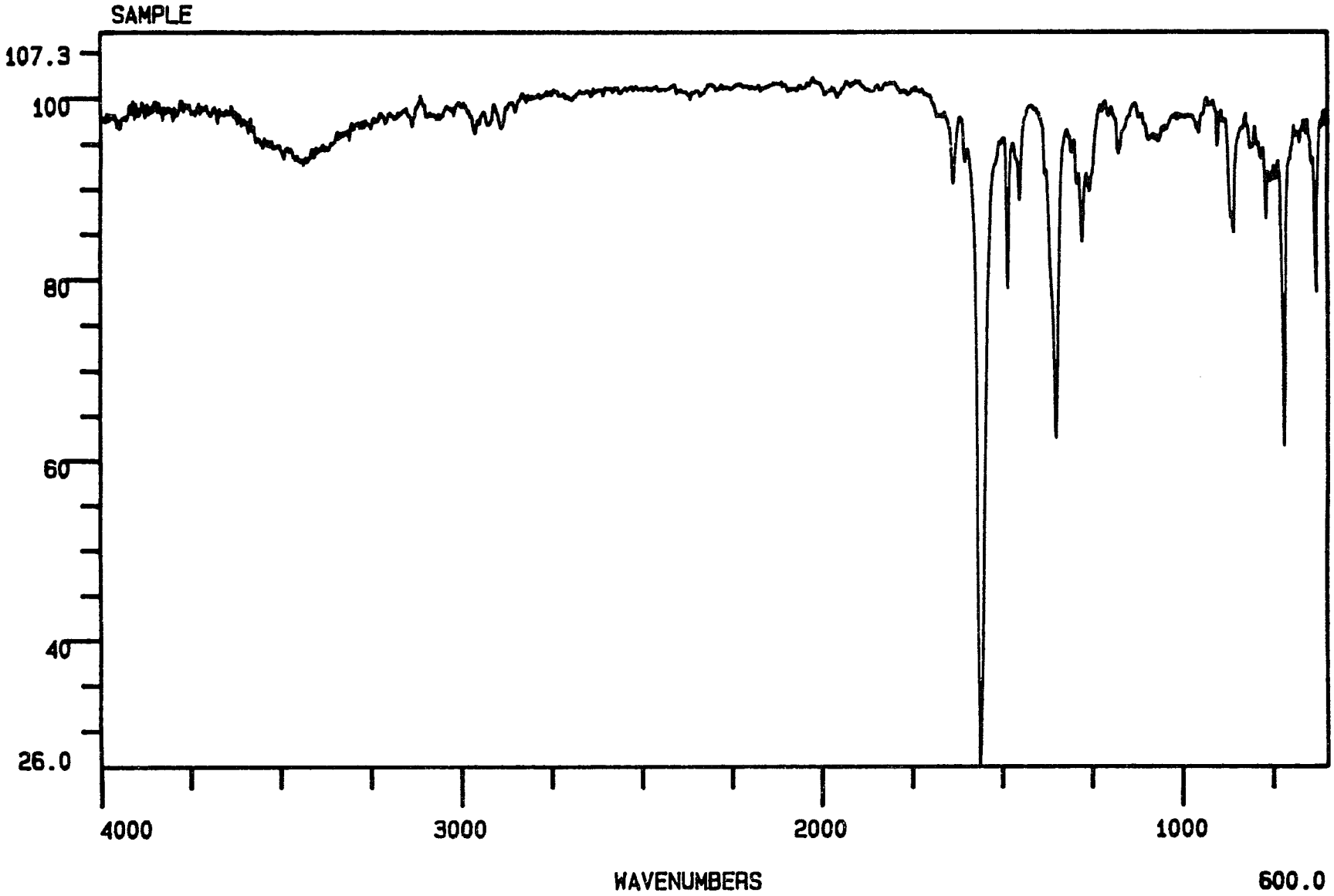


Figure 14. FTIR Spectrum of Cis- 9,10-Dinitro-9,10-dihydroanthracene.

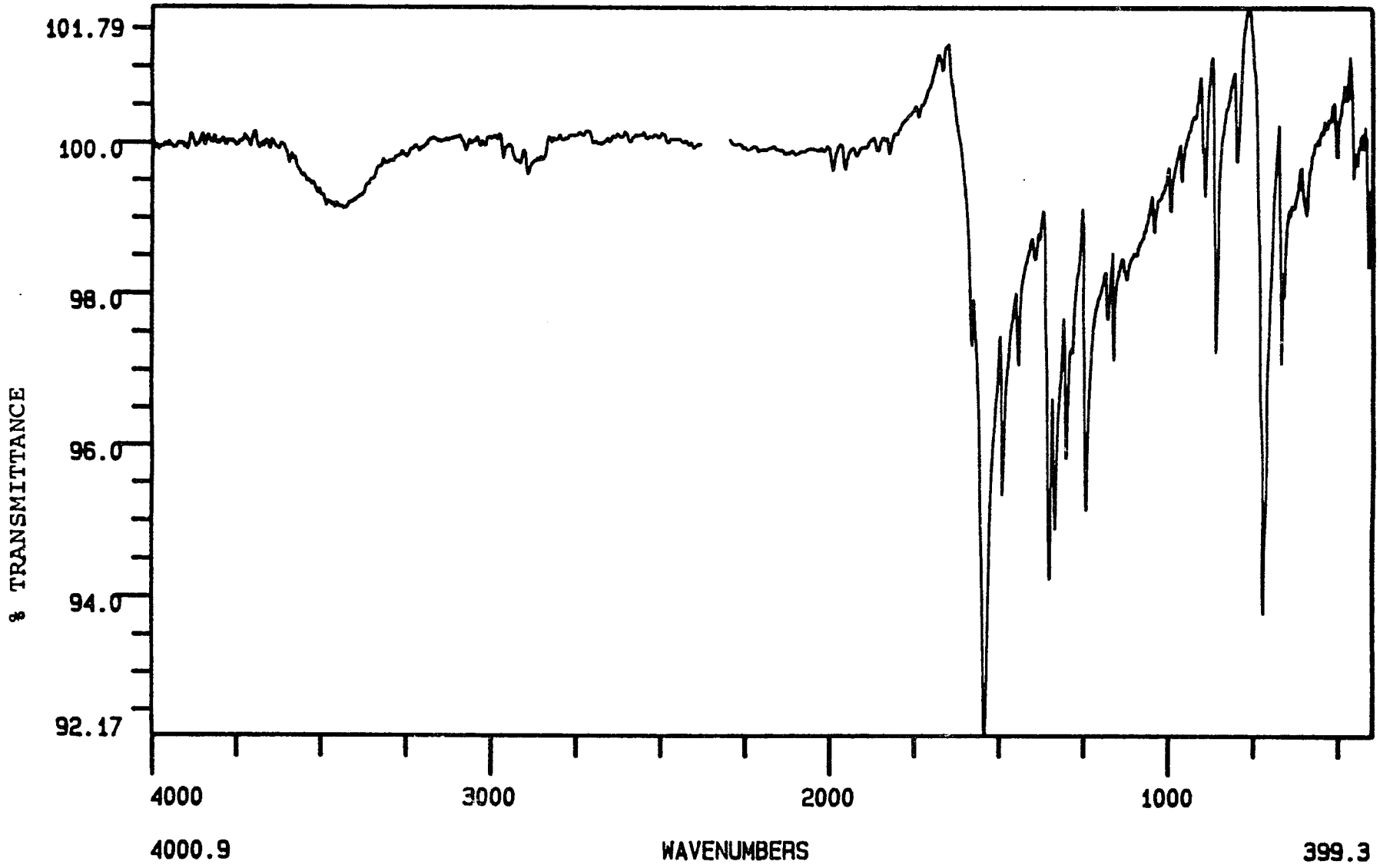


Figure 15. FTIR Spectrum of Trans-9,10-Dinitro-9,10-dihydroanthracene.

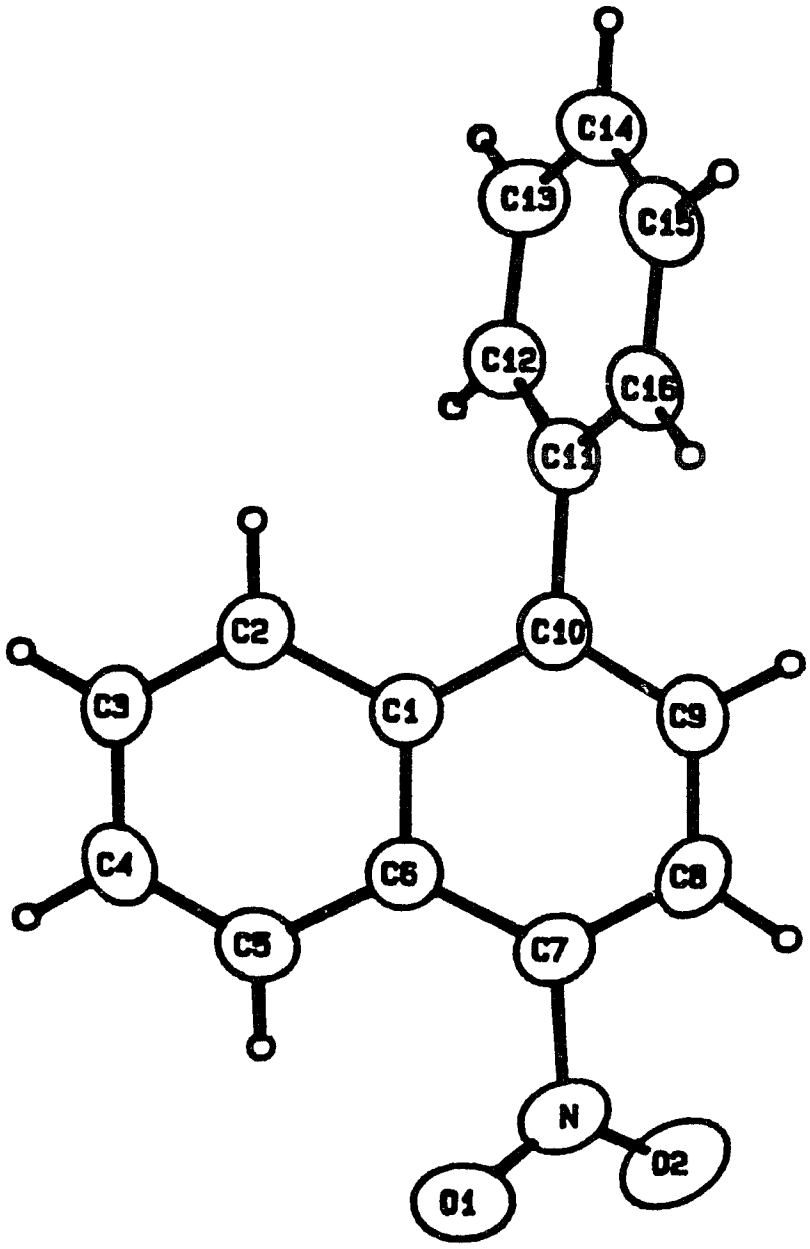


Figure 16. ORTEP Drawing of the X-Ray Structure of 1-Phenyl-4-nitronaphthalene showing the orientation of the phenyl and nitro substituents.

0.44x0.48x0.76 mm on an Enraf-Nonius CAD4 diffractometer equipped with CuKα radiation (λ=1.54184 A) and a graphite monochromator. Crystal data are as follows: $C_{16}H_{11}NO_2$, FW=249.3, monoclinic space group Cc, a=11.878(4), b= 15.477(3), c=7.194(2)A, β=114.19(2)^{o}, V=1206.4(12)A^3, Z=4, d_c= 1.372gcm^{-3}, T=25^{o}C, m=7.0cm^{-1}. One quadrant of data was collected by w-2θ scans within 4^{o}<2θ<150^{o}. Data reduction included corrections for background, Lorentz, polarization, and absorption by ψ scans, with minimum relative transmission coefficient 98.04%. Of 1245 data, 1233 had I>3σ(I) and were used in the refinement. The structure was refined by full-matrix least squares, treating nonhydrogen atoms anisotropically. Hydrogen atoms were located by ΔF and refined isotropically. At convergence, R=0.030 for 215 variables, and the maximum residual density was 0.14eA^{-3}. Tables II, III, IV, V, VI, VII, and VIII list atomic coordinates for nonhydrogen atoms, atomic coordinates for hydrogen atoms, bond distances involving nonhydrogen atoms, bond distances involving hydrogen atoms, bond angles involving nonhydrogen atoms, bond angles involving hydrogen atoms, and anisotropic thermal parameters for 1-phenyl-4-nitronaphthalene, respectively.

Atom	x	y	z	B(A^2)
O1	0	0.1141(1)	0	5.92(4)
O2	0.0608(2)	0.2195(1)	0.2119(3)	6.05(4)
N	0.0817(1)	0.1588(1)	0.1229(2)	4.05(3)
C1	0.3812(1)	0.04508(9)	0.2076(2)	2.69(2)
C2	0.4262(1)	-0.0404(1)	0.2127(2)	2.99(2)
C3	0.3536(1)	-0.1113(1)	0.1931(2)	3.31(3)
C4	0.2306(2)	-0.1001(1)	0.1697(2)	3.51(3)
C5	0.1822(1)	-0.0198(1)	0.1596(2)	3.36(3)
C6	0.2541(1)	0.0550(1)	0.1730(2)	2.83(3)
C7	0.2109(1)	0.1415(1)	0.1613(2)	3.17(3)
C8	0.2834(2)	0.2119(1)	0.1817(3)	3.69(3)
C9	0.4073(2)	0.2003(1)	0.2150(3)	3.58(3)
C10	0.4576(1)	0.1194(1)	0.2317(2)	2.97(3)
C11	0.5911(1)	0.11273(9)	0.2729(2)	3.09(3)
C12	0.6741(2)	0.0668(1)	0.4386(3)	3.57(3)
C13	0.7996(2)	0.0659(1)	0.4798(3)	4.26(4)
C14	0.8419(2)	0.1097(1)	0.3526(3)	4.35(4)
C15	0.7601(2)	0.1546(1)	0.1867(3)	4.06(3)
C16	0.6354(1)	0.1572(1)	0.1478(2)	3.49(3)

Table II. Atomic Coordinates Involving Nonhydrogen Atoms for 1-Phenyl-4-nitronaphthalene.

Atom	x	y	z	B(A^2)
H2	0.510(2)	-0.049(2)	0.237(4)	2.3(4)
H3	0.386(2)	-0.167(1)	0.198(3)	1.7(4)
H4	0.179(3)	-0.149(2)	0.161(4)	3.0(5)
H5	0.103(2)	-0.011(2)	0.147(3)	2.3(4)
H8	0.244(2)	0.266(2)	0.160(3)	2.5(5)
H9	0.456(2)	0.248(2)	0.222(3)	2.3(4)
H12	0.643(2)	0.036(1)	0.529(3)	1.8(4)
H13	0.856(2)	0.033(2)	0.604(4)	2.9(5)
H14	0.925(2)	0.106(2)	0.386(4)	2.8(5)
H15	0.787(2)	0.187(2)	0.087(4)	2.8(5)
H16	0.579(2)	0.189(2)	0.033(3)	2.2(4)

Table III. Atomic Coordinates Involving Hydrogen Atoms for 1-Phenyl-4-nitronaphthalene.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N	1.224(2)	C3	C4	1.412(1)	C10	C11	1.492(1)
O2	N	1.218(2)	C4	C5	1.360(2)	C11	C12	1.391(1)
N	C7	1.469(1)	C5	C6	1.419(1)	C11	C16	1.395(1)
C1	C2	1.422(1)	C6	C7	1.423(1)	C12	C13	1.395(2)
C1	C6	1.434(1)	C7	C8	1.360(2)	C13	C14	1.388(2)
C1	C10	1.431(1)	C8	C9	1.402(1)	C14	C15	1.380(2)
C2	C3	1.366(1)	C9	C10	1.373(1)	C15	C16	1.391(2)

Table IV. Bond Distances Involving Nonhydrogen Atoms for 1-Phenyl-4-nitronaphthalene.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C2	H2	0.95(2)	C8	H8	0.94(2)	C14	H14	0.91(2)
C3	H3	0.94(1)	C9	H9	0.93(2)	C15	H15	1.03(2)
C4	H4	0.96(2)	C12	H12	0.99(1)	C16	H16	0.96(2)
C5	H5	0.92(2)	C13	H13	1.01(2)			

Table V. Bond Distances Involving Hydrogen Atoms for 1-Phenyl-4-nitro-naphthalene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	N	O2	123.0(1)	N	C7	C8	116.17(9)
O1	N	C7	119.4(1)	C6	C7	C8	123.42(9)
O2	N	C7	117.6(1)	C7	C8	C9	119.31(9)
C2	C1	C6	117.54(8)	C8	C9	C10	121.42(9)
C2	C1	C10	122.11(8)	C1	C10	C9	119.40(9)
C6	C1	C10	120.34(8)	C1	C10	C11	122.58(8)
C1	C2	C3	121.99(9)	C9	C10	C11	118.02(8)
C2	C3	C4	119.54(9)	C10	C11	C12	121.86(8)
C3	C4	C5	120.85(9)	C10	C11	C16	119.25(9)
C4	C5	C6	120.86(9)	C12	C11	C16	118.82(9)
C1	C6	C5	119.08(8)	C11	C12	C13	120.5(1)
C1	C6	C7	116.08(8)	C12	C13	C14	119.9(1)
C5	C6	C7	124.81(8)	C13	C14	C15	120.0(1)
N	C7	C6	120.40(9)	C14	C15	C16	120.2(1)
C11	C16	C15	120.6(1)				

Table VI. Bond Angles in Degrees Involving Nonhydrogen Atoms for 1-Phenyl-4-nitronaphthalene.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	C2	H2	119.5(9)	C10	C9	H9	118.6(9)
C3	C2	H2	118.5(9)	C11	C12	H12	119.0(8)
C2	C3	H3	120.4(8)	C13	C12	H12	120.4(8)
C4	C3	H3	120.0(8)	C12	C13	H13	117.1(9)
C3	C4	H4	121(1)	C14	C13	H13	123.0(8)
C5	C4	H4	118(1)	C13	C14	H14	116(1)
C4	C5	H5	122(1)	C15	C14	H14	124(1)
C6	C5	H5	117(1)	C14	C15	H15	122.7(9)
C7	C8	H8	117(1)	C16	C15	H15	117.1(8)
C9	C8	H8	124(1)	C11	C16	H16	120.0(9)
C8	C9	H9	119.9(9)	C15	C16	H16	119.5(9)

Table VII. Bond Angles in Degrees Involving Hydrogen Atoms for 1-Phenyl-4-nitronaphthalene.

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0410(5)	0.0708(9)	0.097(1)	0.0059(6)	0.0122(6)	-0.0008(8)
O2	0.0687(6)	0.0801(9)	0.0905(8)	0.0251(6)	0.0420(5)	-0.0072(7)
N	0.0450(5)	0.0540(7)	0.0569(6)	0.0125(5)	0.0231(4)	0.0078(6)
C1	0.0371(5)	0.0340(6)	0.0312(5)	0.0006(5)	0.0140(4)	-0.0001(5)
C2	0.0405(5)	0.0359(6)	0.0381(5)	0.0031(5)	0.0170(4)	-0.0002(5)
C3	0.0467(6)	0.0324(6)	0.0442(6)	0.0013(5)	0.0160(5)	-0.0004(5)
C4	0.0462(6)	0.0398(6)	0.0452(6)	-0.0101(6)	0.0164(5)	-0.0019(5)
C5	0.0382(5)	0.0465(7)	0.0428(6)	-0.0027(6)	0.0164(4)	-0.0008(6)
C6	0.0379(5)	0.0379(6)	0.0323(5)	0.0009(5)	0.0149(4)	-0.0004(5)
C7	0.0378(6)	0.0420(7)	0.0403(6)	0.0053(5)	0.0158(4)	0.0013(5)
C8	0.0517(7)	0.0346(7)	0.0554(7)	0.0078(6)	0.0233(5)	0.0019(6)
C9	0.0458(7)	0.0335(6)	0.0550(7)	-0.0040(6)	0.0190(5)	-0.0021(6)
C10	0.0396(6)	0.0362(6)	0.0366(5)	-0.0008(5)	0.0153(4)	-0.0004(5)
C11	0.0383(5)	0.0347(6)	0.0431(6)	-0.0040(5)	0.0155(4)	-0.0033(5)
C12	0.0423(6)	0.0431(7)	0.0510(6)	-0.0006(6)	0.0199(5)	0.0050(6)
C13	0.0407(6)	0.0527(9)	0.0633(8)	0.0042(6)	0.0161(6)	0.0069(7)
C14	0.0391(6)	0.0533(9)	0.0744(9)	-0.0035(7)	0.0249(5)	-0.0029(8)
C15	0.0512(6)	0.0462(8)	0.0634(7)	-0.0111(6)	0.0302(5)	-0.0021(6)
C16	0.0447(6)	0.0387(7)	0.0484(6)	-0.0078(6)	0.0183(5)	0.0001(6)

Table VIII. Anisotropic Thermal Parameters for 1-Phenyl-4-nitronaphthalene.

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VITA

Giuseppe Luciano Squadrito was born in Lima, Peru, on December 13, 1959. He attended the San Jose School of the Marist Brothers in Callao, Peru, where he finished his High School education in 1976. Later on, he was admitted to the Catholic University, in Lima, from which he obtained the degree of B.S. with emphasis in Chemistry. He then came as a Fulbright student to Louisiana State University to pursue graduate education. While at Louisiana State University, he married Maria Ines Altbach in November 1984. He is a member of the American Chemical Society, the Phi Lambda Upsilon Honorary Chemical Society, and is currently a candidate for the degree of Doctor of Philosophy in the Department of Chemistry of Louisiana State University.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Giuseppe L. Squadrito

Major Field: Chemistry

Title of Dissertation: "Studies on The Reactions of Polycyclic Aromatic Hydrocarbons with Nitrogen Dioxide in Aprotic Solvents"

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

RC Montelaro

George S. Stanley

Jay C. Means

Robert V. Nauman

Mark L. McLaren

Date of Examination:

October 18, 1988